AD-A078 293 UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT O--ETC F/G 7/3
ORGANOSILICON CHEMISTRY.(U)
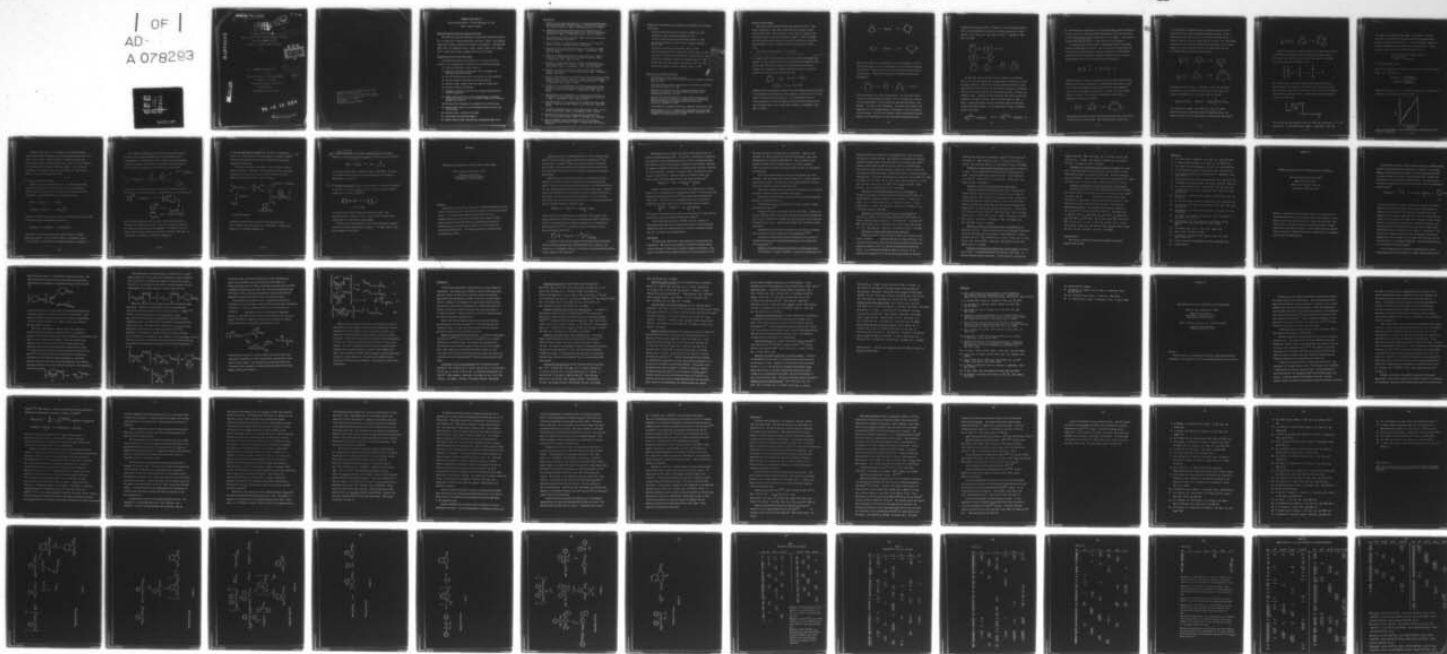SEP 79 W P WEBER   AFOSR-77-3123
UNCLASSIFIED   AFOSR-TR-79-1233   NL

| OF |
AD-
A 078293

AFOSR-TR-79-1233

23 OCT RECD

LEVEL

FINAL SCIENTIFIC REPORT. 1 Oct 76 - 30 Sep 79,

Period covered October 1, 1976 to September 30, 1979

Grant Number AFOSR-77-3123

Air Force Office of Scientific Research

ORGANOSILICON CHEMISTRY.

30 Sep 79

67

Principal Investigator: William P. Weber

Department of Chemistry

University of Southern California

University Park

Los Angeles, California 90007

79 12 10 054

361 555

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is
approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer

ORGANOSILICON CHEMISTRY

Period covered October 1, 1976 to September 30, 1979

Final Scientific Report

Personnel Employed at Various Times on This Grant

The following people were employed as post-doctoral Research Associates: Drs. Tai Shan Fang, Hiroshige Okinoshima, and Bruce I. Rosen. The following people were employed as Research Assistants on this project: Shin-Shin Chen, James Chihi, Sair Hagopian, Bruce I. Rosen, Gowrie N. Soysa, H.S.D. Soysa, Kent P. Steele, Robert Swaim, Dongjaw Tzeng, and Tai Yin Yang.

Equipment Purchased during Grant Period

The following equipment was purchased for use as parts for high pressure liquid chromatography system which are functioning quite well.

1) Strip Chart Recorder, Fisher Scientific

2) Laboratory Data Control (LDC) Model 709 Pulse Dampener for existing Milton Roy Mini-pump

3) LDC 1107 Refracto-monitor with low index prism, Cole Scientific

4) LDC Cell Assembly (high-index prism) Cole Scientific

5) Variable Volume, Universal Injector (7000 psi rated), Altex

6) Fraction collector FC-100 Gilson

7) A Rheodyne injector for the HPLC was purchased through Applied Sciences Laboratories

8) A high pressure pump for a liquid chromatograph: Altex model 110-00 which permits delivery of solvents at 5000 psi was obtained through Cole Scientific

The following other equipment was purchased for use on this grant:

9) 450 Watt power supply for use with medium pressure mercury lamp, Conrad Hanovia

10) Rotavapor Buchi, Van Waters and Rogers

11) Vacuum Pump, Van Waters and Rogers

12) Hewlett Packard flame ionization gas chromatograph model 5711A

Publications

1. Synthesis of 4,5-Dihydrobenz[b]furans, 4,5-Dihydrobenzo[b]thiophenes, and 4,5-Dihydroindols - Vacuum Pyrolysis - Electrocyclic Reactions, B.I. Rosen and William P. Weber, Tetrahedron Letters, 151 (1977).

2. A New Route to Dimethylsilanone [$(CH_3)_2Si=O$]; Deoxygenation of Dimethylsulfoxide by Dimethylsilylene, H.S.D. Soysa, H. Okinoshima, and William P. Weber, J. Oragnometal. Chem., 133, C-17 (1977).

3. Cyclization via Pyrolysis, William P. Weber and Brice Irwin Rosen, Chemical Technology, 690 (1977).

4. Facile Reduction of Sulfoxides by Disilthianes, H.S.D. Soysa and William P. Weber, Tetrahedron Letters, 235 (1978).

5. Photolysis of Aryl Substituted Disilanes in the Presence of DMSO, Hiroshige Okinoshima and William P. Weber, J. Organometal. Chem., 149, 279 (1978).

6. Insertion of Methylphenylsilylene in Cyclic Siloxanes - Effect of Ring Size on Siloxane Reactivity, H. Okinoshima and W.P. Weber, J. Organometal. Chem., 150, C25 (1978).

7. Photolysis of Heptamethyl-2-phenyltrisilane and Octamethyl-2,3-diphenyltetrasilane in the Presence of DMSO, Hiroshige Okinoshima and William P. Weber, J. Organometal. Chem., 155, 165 (1978).

8. Reduction of Sulfoxides by Dichlorocarbene under Phase Transfer Catalysis Conditions, H.S.D. Soysa and William P. Weber, Tetrahedron Letters, 1969 (1978).

9. Pyrolysis of Hexamethylcyclotrisilthiane and Tetramethylcyclodisilthiane in the Presence of Cyclic Siloxanes. Evidence for the Intermediacy of Dimethylsilathione [$(CH_3)_2Si=S$], H.S.D. Soysa and William P. Weber, J. Organometal. Chem., 165, C1 (1979).

10. Pyrolysis of 1,1,2,2-Tetramethyl-1,2-Disila-3,6-Dithiacyclohexane - Evidence for Dimethylsilathione [$(CH_3)_2Si=S$] Intermediate, H.S.D. Soysa, I.N. Jung, and W.P. Weber, J. Organometal. Chem., 171, 177 (1979).

11. Reinvestigation of the Photolysis of Aryl-Substituted Disilanes in The Presence of Dimethylsulfoxide, H.S. Dilanjan Soysa and William P. Weber, J. Organometal. Chem., 173, 269 (1979).

12. Photo-Oxidation of 1,1,1-Trimethyl-2,2,2-Triphenyldisilane by DMSO, Robert E. Swaim and William P. Weber, J. Am. Chem. Soc., 101, 5703 (1979).

13. Insertion of Dimethylsilylene into O-H and N-H Single Bonds, Tai-Yin Yang Gu and William P. Weber, J. Oragnometal. Chem., in press.

14. Mechanism of the Reactions of Dimethylsilylene with Oxetanes, Tai-Yin Yang Gu and William P. Weber, J. Am. Chem. Soc., submitted.

15. Mass Spectrometry of Aryl-substituted Di- and Tri-Siloxanes, Robert E. Swaim and William P. Weber, J. Organic Mass Spectrometry, submitted.

Seminars were presented on work supported by the AROSR at the following institutions:

California State University at Fullerton, February 24, 1977

Pennsylvania State University, November 10, 1977

California State University at Northridge, November 4, 1977

Grace Chemical Company, Research Center, Columbia, Maryland, May 31, 1978

University of Puerto Rico-Rio Piedras, April 2, 1979

Florida State University at Tallahassee, Florida, April 5, 1979

University of Virginia, Charlottesville, Virginia, April 9, 1979

University of Maryland, College Park, Maryland, April 10, 1979

Temple University, Philadelphia, Pennsylvania, April 12, 1979

University of Delaware, Newark, Delaware, April 13, 1979

Papers Given at Scientific Meetings

Invited Lecturer Kipping Award Symposium
National Meeting of the American Chemical Society, Anaheim, California
March 17, 1978

Fifth International Symposium on Organosilicon Chemistry, Karlsruhe, West Germany, August 14-18, 1978

Reduction of Sulfoxide by Dichlorocarbene under Phase Transfer Catalysis Conditions at Pacific Conference on Chemistry and Spectroscopy, September 28, 1978

Organized and Chaired Symposium on "Phase Transfer Catalysis" at Pacific Conference on Chemistry and Spectroscopy at the American Chemical Society Western Regional Meeting, San Francisco, California, September 28, 1978.

XIII Organosilicon Symposium, Ann Arbor, Michigan, March 30-31, 1979

Photo-oxidation of 1,1,1-Trimethyl-2,2,3-Triphenyldisilane by DMSO at the American Chemical Society National Meeting, Washington, D.C., September 1979 (presented by R.E. Swaim)

Research Accomplishments

Most of our work has been published (see publication list). Often results related to a single goal or objective are the subject of more than one publication. For this reason, I will attempt to summarize the scientific success of the past three years (October 1, 1976 to September 30, 1979) achieved with the support of the Air Force Office of Scientific Research AROSR 77-3123. I hope this will bring our work into clearer focus.

Our results can be divided in six main areas.

The following studies are summarized:

A.) Several aspects of the chemistry of polysilane-polysulfides have been studied. We have determined that the easily established thermal equilibration of hexamethylcyclotrisilthiane and tetramethylcyclodisilthiane involves the intermediacy of dimethylsilathione $[(CH_3)_2Si=S]$ a reactive species possessing a silicon-sulfur double bond.
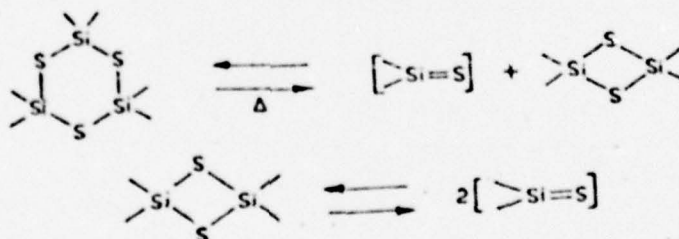
Dimethylsilathione generated by pyrolysis of either hexamethylcyclotrisilthiane or tetramethylcyclodisilthiane has been trapped by insertion into Si-O single bonds of hexamethylcyclotrisiloxane or 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane to yield new organosilicon heterocycles possessing Si-O and Si-S single bonds. H.S.D. Soysa and W.P. Weber, J. Organometal. Chem. 165, C1 (1979).

→ to p. 4
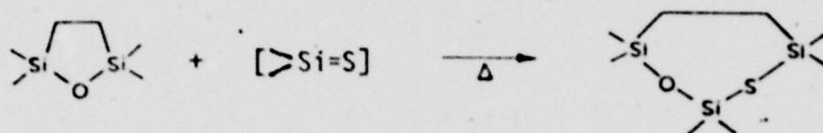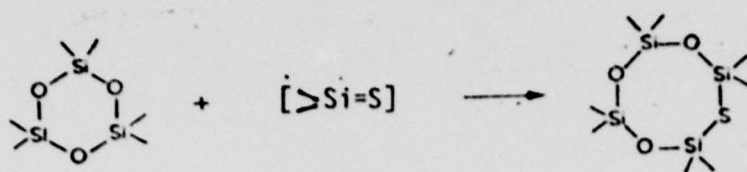
We have also found that the pyrolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane to yield 1,1-dimethyl-1-sila-2,6-dithiacyclopentane 1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-dithiacyclopentane and ethylene in equal amounts involves the intermediacy of dimethylsilathione as an intermediate.
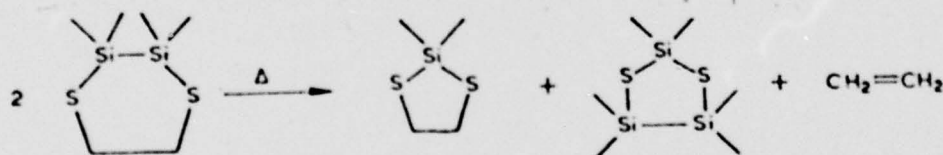
The reaction occurs via a three step mechanism. The first step involves a $[\pi 2s, \pi 2s, \pi 2s]$ cycloreversion reaction of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane to yield ethylene and two dimethylsilathione intermediates. This step is rate determining. The second step is head to tail dimerization of the dimethylsilathione intermediates to yield tetramethylcyclodisilthiane. The third step involves a rapid redistribution reaction between 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane and tetra-

methylcyclodisilthiane to yield 1,1-dimethyl-1-sila-2,5-dithiacyclopentane and 1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-dithiacyclopentane in equal amounts. H.S.D. Soysa, I.N. Jung, and W.P. Weber, J. Organometal. Chem. 171, 177 (1979).
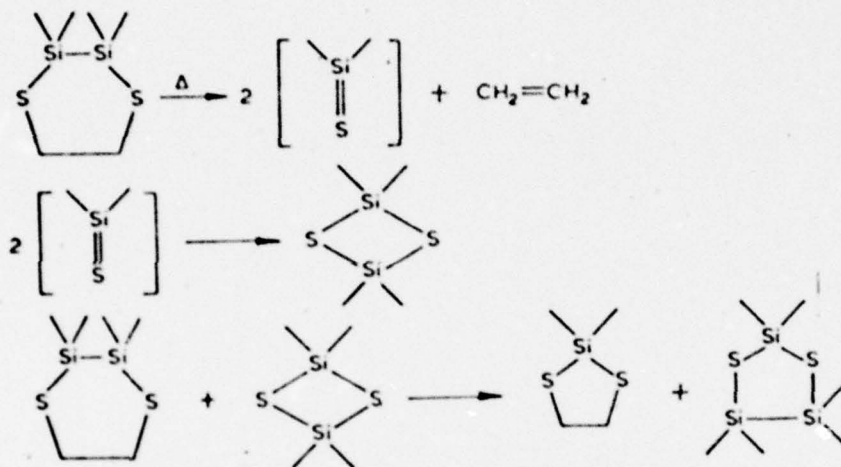
We have shown that sulfoxides are easily reduced by disilthianes. This is one of the few applications of organosulfur derivatives of silicon to organic synthesis. Specifically either hexamethyldisilthiane or hexamethylcyclotrisilthiane reacts with sulfoxides in chloroform, or methylene chloride to give high yields of the corresponding sulfides, siloxanes, and elemental sulfur. Advantages of this method are that yields are high, the conditions are neutral and milds, and the reaction rates are rapid. A number of functional groups--such as β-keto and α-chloro are tolerated by these disilthiane reagents. H.S.D. Soysa and W.P. Weber, Tetrahedron Letters, 235 (1978).
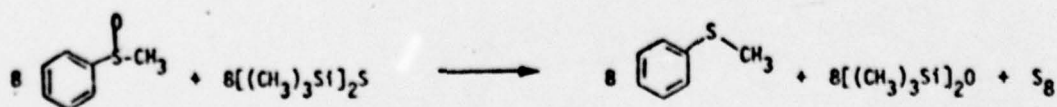
B.) The photochemical generation of silicon-oxygen doubly bonded intermediates and the study of the insertion of these intermediates into Si-O single bonds of siloxanes have been primary research goals of this project. Such insertion

→ to p. 8

reaction might provide new ways to functionalize silicone polymers.

We have generated dimethylsilanone, methylphenylsilanone and diphenyl-silanone in photochemical reactions. Our first success in this project was the finding that dimethylsilylene generated by photolysis of dodecamethyl-cyclohexasilane would deoxygenate dimethyl sulfoxide, as well as various tertiary amine oxides to yield dimethylsilanone [$(CH_3)_2Si=O$].

During the course of this work we unexpectedly found that dimethylsilylene would insert into Si-O single bonds of hexamethylcyclotrisiloxane to yield 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane. This is the first example of insertion of a silylene into an Si-O single bond of a siloxane. H.S.D. Soysa, H. Okinoshima, and W.P. Weber, J. Organometal. Chem. 133, C17 (1977).
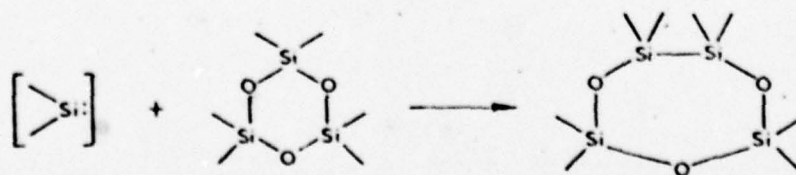
Unfortunately, the scope of this insertion reaction was found to be limited to angle strained siloxane bonds. Thus dimethylsilylene inserts into

- 4 -

Si-O single bonds of hexamethylcyclotrisiloxane but not into the less
strained Si-O single bonds of octamethylcyclotetrasiloxane. Methyl-
phenylsilylene was found to be less reactive than dimethylsilylene in
insertion reactions into Si-O single bonds of siloxanes. Thus methylphenyl-
silylene will insert into the strained Si-O single bond of 1,1,3,3-tetra-
methyl-2-oxo-1,3-disilacyclopentane but not into the less strained
Si-O single bonds of hexamethylcyclotrisiloxane.
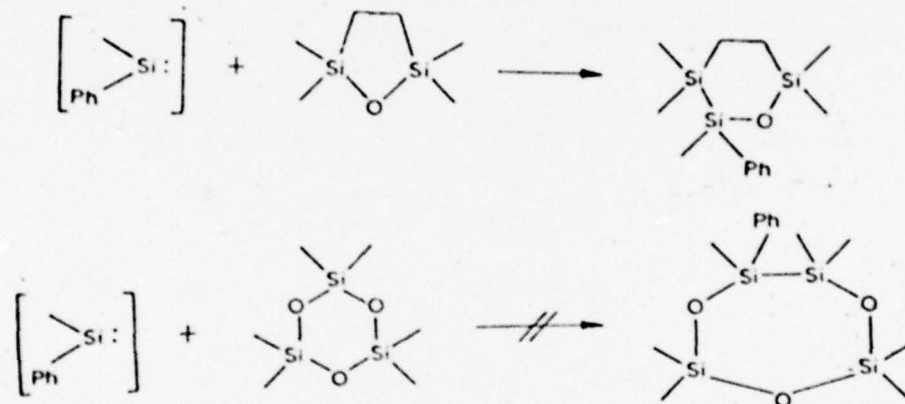
H. Okinoshima and W.P. Weber, J. Organometal. Chem. 150, C25 (1978).
Fortunately, no such limitation has been found in the insertion of
silanone intermediates into Si-O single bonds of siloxanes.

$$(CH_3)_3Si-O-Si(CH_3)_3 \;+\; [\phi_2Si{=}O] \;\rightarrow\; (CH_3)_3Si-O-\underset{\phi}{\overset{\phi}{Si}}-O-Si(CH_3)_3$$
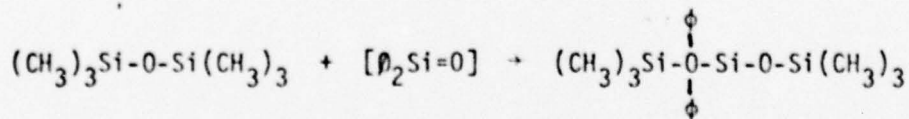
R.E. Swaim and W.P. Weber, J. Am. Chem. Soc., 101, 5703 (1979).
Insertion reactions of dimethylsilanone, methylphenylsilanone, and
diphenylsilanone into Si-O single bonds of siloxanes have been studied.
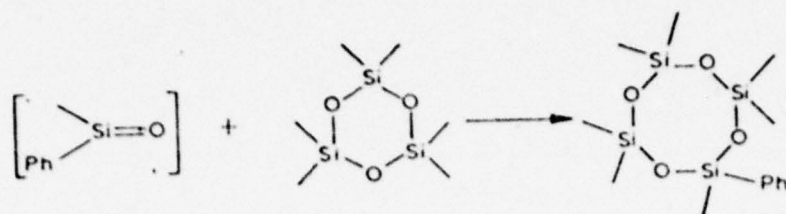
We have also found that photo-oxidation of aryl substituted disilanes in the presence of dimethyl sulfoxide proceeds by two major pathways. One involves direct oxidation of the Si-Si single bond of the disilane to yield a disiloxane and dimethyl sulfide.
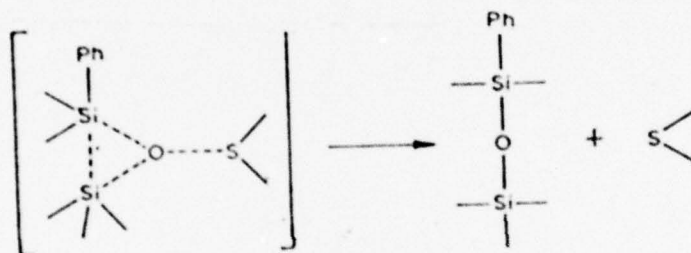
The second involves nucleophilic attack by the oxygen of DMSO on the aryl substituted silyl center of the photoexcited disilane which causes the aryl group to migrate to the other silyl center resulting in formation of an aryl substituted monosilane, a silanone intermediate and dimethyl-sulfide in a single step.
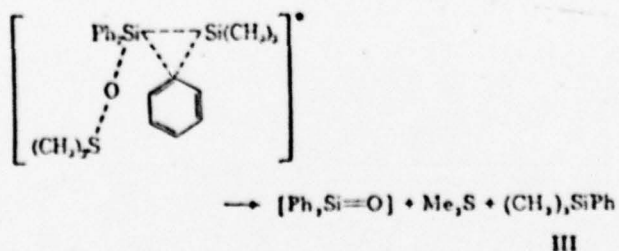
This reaction has been studied in detail for both aryl substituted di-, tri- and tetrasilanes. H. Okinoshima and W.P. Weber, J. Organometal. Chem. 149,

279 (1978), H. Okinoshima and W.P. Weber, J. Organometal. Chem. 155, 165 (1978).   The fact that the quantum yield for these photochemical oxidation reactions are quite high ($\phi \approx .5$) is of particular importance. Silanone intermediate can be generated with high efficiency.   Kinetic data was found to fit the following mechanistic scheme.

$$I + h\nu \xrightarrow{\ k_{h\nu}\ } I^* + Me_2SO \xrightarrow{\ k_2\ } complex \longrightarrow products$$

$$\underbrace{\hspace{3cm}}_{k_{deact}} \quad \searrow^{k_1} \quad decomposition$$
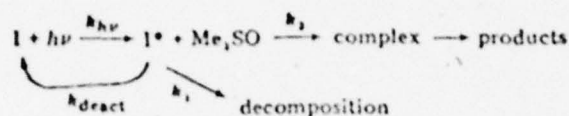
I = aryl substituted disilane.

The rate of disappearance of DMSO was found to obey the kinetic expression below. I_a = light intensity.

$$-d[Me_2SO]/dt = \frac{k_2 I_a [Me_2SO]}{k_1 + k_{deact} + k_2 [Me_2SO]}$$

$$-dt/d[Me_2SO] = \frac{k_{deact} + k_1}{k_2 I_a [Me_2SO]} + \frac{1}{I_a}$$

A Stern-Volmer plot of $1/\phi$ versus $1/[DMSO]$ was found to be linear with an intercept of approximately unity--as predicted.
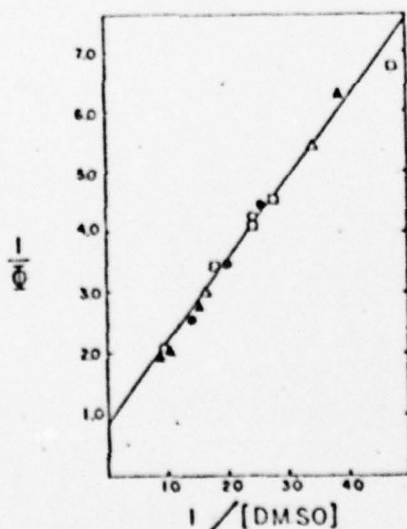
Stern-Volmer dependence on Me_2SO concentration of the quantum yield for reaction I with Me_2SO.

Further in the case of 1,1,1-trimethyl-2,2,2-triphenyldisilane a major solvent effect on the ratio of the two photo-oxidation processes was found. Thus in furan solvent formation of diphenylsilanone was the major process. While in tetrahydrofuran, the formation of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane was the dominant pathway. H.S.D. Soysa and W.P. Weber, J. Organometal. Chem. <u>173</u>, 269 (1979), R.E. Swaim and W.P. Weber, J. Am. Chem. Soc. <u>101</u>, 5703 (1979).

C. Novel reactions of silylenes.

Dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane has been found to insert efficiently into O-H single bonds of water and alcohols as well as into N-H angle bonds of amines to yield respectively alkoxydimethylsilanes and aminodimethylsilanes.

$$R\text{-}O\text{-}H \ + \ [(CH_3)_2Si\text{:}] \ \rightarrow \ R\text{-}O\text{-}\overset{|}{\underset{|}{Si}}\text{-}H$$

$$(CH_3)_3NH_2 \ + \ [(CH_3)_2Si\text{:}] \ \rightarrow \ (CH_3)_3\text{-}\overset{H}{N}\text{-}\overset{|}{\underset{|}{Si}}\text{-}H$$
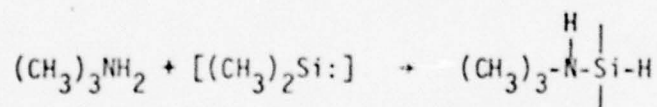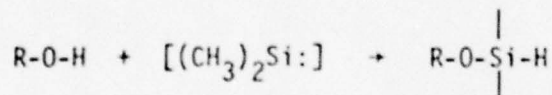
Insertion of dimethylsilylene into O-D bands of deuterated alcohols provides an efficient route to alkoxydimethylsilane-Si-d_1.

$$CH_3\text{-}CH_2\text{-}O\text{-}D \ + \ [(CH_3)_2Si\text{:}] \ \rightarrow \ CH_3\text{-}CH_2\text{-}O\text{-}\overset{|}{\underset{|}{Si}}\text{-}D$$
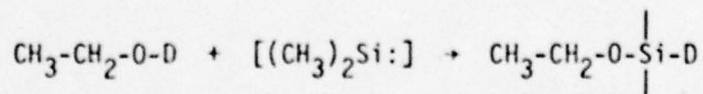
This reaction should provide the most economical method to prepare deuterated silanes. T.Y.Y. Gu and W.P. Weber, J. Organometal. Chem., in press (1979). (A pre-print of the manuscript appears as Appendix I).

The reaction of dimethylsilylenes with oxetanes has been found to give high yield of allyloxydimethylsilane and 2,2-dimethyl-1-oxa-2-silacyclopentane. The formation of these products results from decomposition of an initial 1,2-zwitterionic intermediate formed coordination of the electrophilic dimethylsilylene with the oxygen of oxetane.

$$\square_O \quad + \quad [(CH_3)_2Si:] \quad \longrightarrow \quad \left[\text{1,2-zwitterionic intermediate} \right] \quad \nearrow \quad CH_2=CH-CH_2-O-Si-H$$
$$\searrow \quad \text{(2,2-dimethyl-1-oxa-2-silacyclopentane)}$$
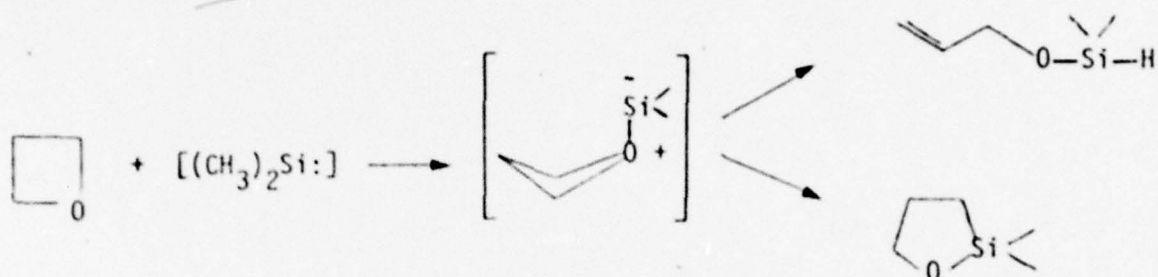
Similar results have been obtained in reactions of dimethysilylene with 2-methyloxetane, 2,2-dimethyloxetane, 3,3-dimethyloxetane and 2-vinyloxetane.

$$\text{(2-vinyloxetane)} \quad + \quad [(CH_3)_2Si:] \quad \longrightarrow \quad \left[\text{intermediate} \right] \longrightarrow \left[\text{intermediate} \right] \longrightarrow \text{(products)}$$
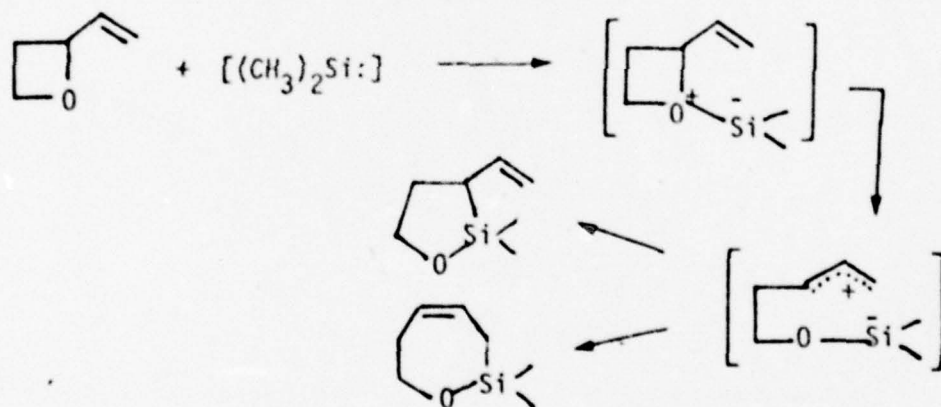
While dimethylsilylene does not react with strained aliphatic ethers-- it may well for complexes with them. Clearly the influence of solvation on silylene reactivity needs to be determined. This paper by T.Y.Y. Gu and W.P. Weber has been submitted to the Jour. of the Amer. Chem. Soc. for consideration. A preprint is included as Appendix II.

D.) ~~Work has been done to elucidate~~ the mass spectral fragmentation patterns of several classes of aryl substituted disiloxanes. Isotopic labelling and peak matching were used to substantiate the proposed fragmentation mechanisms.

Siliconium ions dominate the spectra. Loss of neutral fragments from the M-15 ions is important. For example, the M-15 ions of phenyl-pentamethyldisiloxane looses methane, dimethylsilanone and phenyl-methylsilanone to yield daughter siliconium ions.
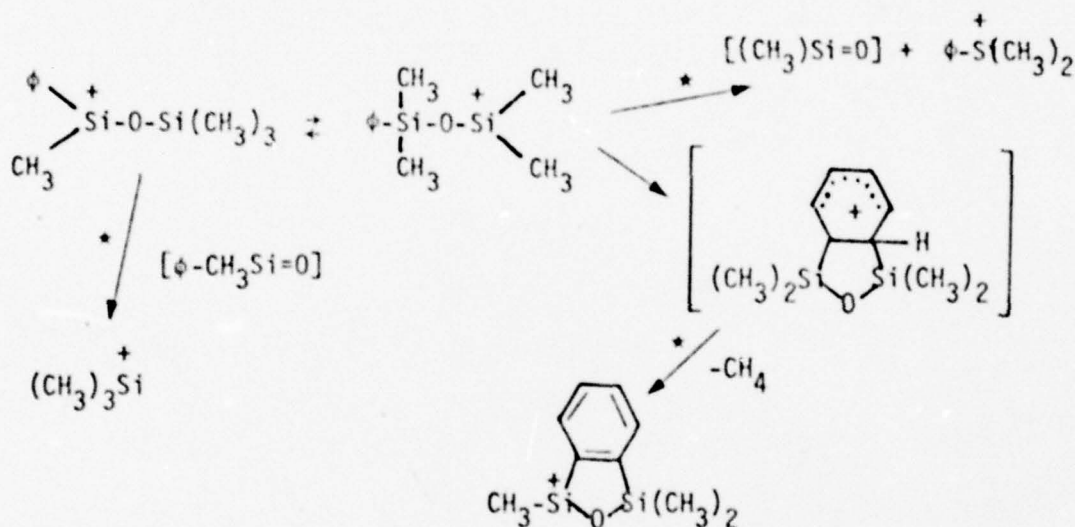
* metastable observed

A manuscript reporting these results has been submitted to the Jour. of Organic Mass Spectrometry for consideration. A copy of this manuscript is included as Appendix III.

generation of

(E.) ~~We have found that~~ dichlorocarbene ~~generated~~ under Phase Transfer Catalysis conditions efficiently deoxygenates sulfoxides to yield sulfides.

$$\phi_2\text{S-O} + [:\text{CCl}_2] \longrightarrow \phi_2\text{S} + \underset{\text{Cl}}{\overset{\overset{\displaystyle O}{\|}}{\text{C}}}\text{Cl}$$

H.S.D. Soysa and W.P. Weber, Tetrahedron Letters 1969 (1978). This work is related to the previously discussed deoxygenation of sulfoxides by disilthianes--see section A.

and (F.) ~~We have examined the~~ gas phase vacuum pyrolysis of several five membered heterocyclic-1,2-butadienes. Electrocyclic reaction yields 4,5-dihydro-benzo-furans, thiophenes and indoles.

$$X = O, S, N\text{-}CH_3$$
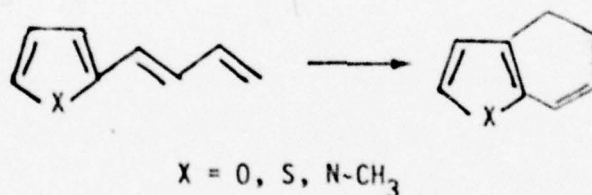
B.I. Rosen and W.P. Weber, Tetrahedron Letters 151 (1977). This reaction provides an efficient route to these partially reduced hetero-cycles which are inaccessible by other methods.

Finally, we have reviewed our work on similar electrocyclic pyrolysis reactions to prepare dihydroaromatic compounds. W.P. Weber and B.I. Rosen, Chem. Tetrahedron. 690 (1977).

INSERTION OF DIMETHYLSILYLENE INTO O-H AND N-H SINGLE BONDS

Tai-Yin Yang Gu and William P. Weber*

Department of Chemistry
University of Southern California
Los Angeles, California 90007

Abstract

Dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane, inserts efficiently into O-H single bonds of alcohols to yield alkoxydimethylsilanes. Use of ethanol-O-d_1 yields ethoxydimethylsilane-Si-d_1. Dimethylsilylene also inserts into O-H single bonds of water or D_2O to yield respectively tetramethylsiloxane or tetramethylsiloxane-Si_2-d_2. Dimethylsilylene also inserts into N-H bonds of 1° and 2° amines to yield aminodimethylsilanes. This reaction provides an efficient route to difunctional silanes.

Insertion reactions of dimethylsilylene into silicon-hydrogen single bonds,[1,2] and into silicon-oxygen single bonds of alkoxysilanes,[3,4] and strained cyclic siloxanes[5,6] have been previously reported. We should like to report insertion reactions of dimethylsilylene into both O-H and N-H single bonds which provide efficient methods to generate difunctional organosilanes.

Dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[4] in a solution of ether and ethanol yields ethoxydimethylsilane (87%).[7] Yields are reported based on the generation of two dimethylsilylenes for each dodecamethylcyclohexasilane which is the limiting reagent. Similar reaction of dimethylsilylene with ethanol-O-d_1 yields ethoxydimethylsilane-Si-d_1 (84%). We believe this procedure, which does not involve reduction with lithium aluminum deuteride, may provide the most efficient and economical route to functional deuterium labelled silanes.

$$[(CH_3)_2Si:] + CH_3CH_2\text{-}O\text{-}D \rightarrow (CH_3)_2\underset{D}{Si}\text{-}O\text{-}CH_2CH_3$$
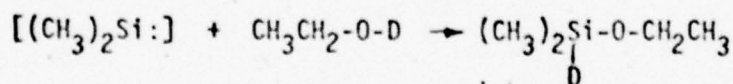
Similar reactions of dimethylsilylene with methanol and t-butanol yield methoxydimethylsilane (89%)[8] and t-butoxydimethylsilane (85%)[9] respectively. Likewise, methylphenylsilylene generated by photolysis of octamethyl-2,3-diphenyltetrasilane[10,11] in a solution of ether and t-butanol yields t-butoxymethylphenylsilane (77%).

$$\begin{bmatrix} CH_3 \\ \phi \end{bmatrix} Si: \Big] + (CH_3)_3C\text{-}O\text{-}H \longrightarrow \begin{matrix} CH_3 \\ \phi \end{matrix} Si \begin{matrix} H \\ O\text{-}C(CH_3)_3 \end{matrix}$$
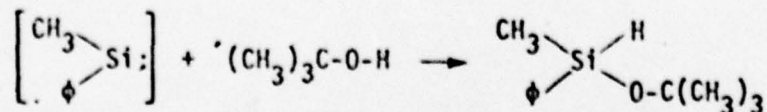
It should be noted that the reaction of difluorosilylene with methanol did not yield the expected adduct, methoxydifluorosilane, although it was proposed as an intermediate involved in the formation of dimethoxydifluorosilane, a minor product of this reaction.[12]

Dimethylsilylene also inserts into the O-H single bonds of water to yield tetramethyldisiloxane (85%). The reaction is carried out by photolysis of a solution of dodecamethylcyclohexasilane in ether saturated with water. The efficiency of this reaction makes it imperative that anhydrous conditions be rigorously maintained if reaction of dimethylsilylene with other substrates are to be successful. If water is replaced by D_2O, tetramethyldisiloxane-Si_2-d_2 is produced (82%). Analogous reaction of difluorosilylene with water to yield tetrafluorodisiloxane has been previously observed.[13]

$$[(CH_3)_2Si:] + D_2O \longrightarrow (CH_3)_2\underset{D}{Si}{-}O{-}\underset{D}{Si}(CH_3)_2$$

Likewise, dimethylsilylene inserts into N-H single bonds of secondary amines, such as diethylamine and 2,2-dimethylaziridine[14] to yield respectively N,N-diethylaminodimethylsilane (81%)[15] and 2,2-dimethylaziridinodimethylsilane (85%). No insertion of the dimethylsilylene into the strained carbon-nitrogen single bonds of the 2,2-dimethylaziridine was observed.
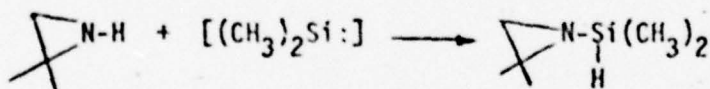
The insertion of dimethylsilylene into one of the primary N-H single bonds of t-butylamine yields N-t-butylaminodimethylsilane (86%).[16]

On the other hand, photolysis (2537 Å) of an ether solution of dodecamethylcyclohexasilane and n-propanethiol did not yield any n-propylthiodimethylsilane, the expected product of insertion of dimethylsilylene into the S-H single bond of n-propanethiol.

Experimental

IR spectra were determined as CCl_4 solutions on a Perkin-Elmer 281 spectrometer. NMR spectra were recorded on a Varian XL-100 spectrometer using 5% solutions in $CDCl_3$ with an internal standard of chloroform. Mass spectra were determined on a duPont 21-492 at an ionizing voltage of 70 eV.

UV spectra were run on a Beckman Acta M spectrometer. Samples of all compounds for spectra analysis were purified by preparative vapor phase chromatography on a Hewlett Packard F&M 700. Yields of products were determined by GLPC with cyclooctane added as an internal standard. Yields are based on two moles of dimethylsilylene per mole of dodecamethylcyclohexasilane.

All of the starting materials and most of the products are known compounds. They had physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

Ether and tetrahydrofuran were purified by distillation from a solution of sodium benzophenone ketyl immediately prior to use.

Diethylamine and t-butylamine were distilled from potassium hydroxide pellets immediately prior to use.

2,2-Dimethylaziridine was prepared from 2-amino-2-methyl-1-propanol by the method of Meyers.[14]

Absolute ethanol was used without further purification. Methanol and ethanol-O-d_1[17] were refluxed over calcium oxide and were distilled immediately prior to use. t-Butanol was refluxed over calcium hydride and was distilled immediately prior to use. Deuterium oxide (D_2O)[17] was used without further purification.

Dodecamethylcyclohexasilane was prepared by the reaction of dimethyldichlorosilane and excess lithium metal in tetrahydrofuran.[18,19]

Octanethyl-2,3-diphenyltetrasilane was prepared by the reaction of trimethylchlorosilane and methylphenyldichlorosilane with lithium metal in tetrahydrofuran.[11]

Photolysis of dodecamethylcyclohexasilane in 2,2-dimethylaziridine.

The following is a typical procedure. A solution of dodecamethylcyclo-

-4-

hexasilane (105 mg, 0.3 mmol) in 2,2-dimethylaziridine (1.42 g, 20 mmol) was placed in a quartz nmr tube. The solution was deoxygenated by bubbling purified nitrogen through it for 10 min prior to irradiation with a 450 W medium pressure Hanovia Hg lamp for 90 min at 5°C in an ice/water bath. GLPC analysis of the resulting colorless solution on a 1/4" x 7' 20% SE-30 on Chromosorb W 60/80 mesh column indicated 85% yield of 2,2-dimethylaziridino-dimethylsilane. It had the following spectral properties: IR Si-H 2060 cm^{-1}. NMR δ 4.27 (sept. 1H, J = 3 Hz), 1.65 (s, 2H), 1.24 (s, 6H), 0.19 (d, 6H, J = 3 Hz). Mass spectrum: Parent m/e = 129 (54%), calcd. $C_6H_{15}NSi$ 129.097; found 129.097; P-1 m/e = 128 (78%), P-15 m/e = 114 (100%).

Photolysis of dodecamethylcyclohexasilane in diethylamine was carried out as above to yield N,N-diethylaminodimethylsilane[15] (81%). It had the following spectral properties: IR Si-H 2120 cm^{-1}. NMR δ 4.27 (sept., 1H, J = 3 Hz), 2.79 (q, 4H, J = 7 Hz), 0.97 (t, 6H, J = 7 Hz), 0.095 (d, 6H, J = 3 Hz). Mass spectrum: Parent m/e = 131 (20%), P-1 m/e = 130 (8%), P-15 m/e = 116 (100%).

Photolysis of dodecamethylcyclohexasilane in t-butylamine was carried out as above to yield N-t-butylaminodimethylsilane[16] (86%). It had the following spectral properties: IR N-H 3395 cm^{-1}, Si-H 2110 cm^{-1}. NMR δ 4.49 (d sept., 1H, J = 2.75 and 3 Hz), 1.11 (s, 9H), 0.097 (d, 6H, J = 3 Hz). Mass spectrum: Parent m/e = 131 (21%), P-15 m/e = 116 (100%).

Photolysis of dodecamethylcyclohexasilane with water.

Dodecamethylcyclohexasilane (70 mg, 0.2 mmol) was dissolved in ether (1.18 g, 16 mmol) saturated with water in a quartz NMR tube. This solution was photolyzed as above and the resulting colorless solution was analyzed by GLPC on a 1/4" x 12' 20% SE-30 on Chromosorb W 60/80 mesh column. 1,1,2,2-Tetramethyldisiloxane (85%) was isolated. It was identified by comparison of its IR and NMR spectral properties and GLPC

retention time with those of an authentic sample.[20] IR Si-H 2120 cm^{-1}, Si-O 1055 cm^{-1}. NMR δ 4.66 (sept., 2H, J = 2.8 Hz), 0.17 (d, 6H, J = 2.8 Hz). Mass spectrum: Parent-1 m/e = 133 (72%), P-15 m/e = 119 (100%).

Photolysis of dodecamethylcyclohexasilane with D_2O was carried out as above. 1,1,2,2-Tetramethyldisiloxane-Si_2-d_2 was obtained in 82% yield. It had the following spectral properties: IR Si-D 1550 cm^{-1}, Si-O 1055 cm^{-1}. NMR δ 0.17 (s). Mass spectrum: Parent-2 m/e = 134 (52%), P-15 m/e = 121 (100%).

Photolysis of dodecamethylcyclohexasilane with ethanol.

A mixture of dodecamethylcyclohexasilane (70 mg, 0.2 mmol) and ethanol (230 mg, 5 mmol) was dissolved in ether (1.11 g, 15 mmol) in a quartz NMR tube. This solution was photolyzed as above. Analysis of the resulting colorless solution by GLPC on a 1/4" x 12' 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of ethoxydimethyl-silane (87%).[7] It had the following spectral properties: IR Si-H 2110 cm^{-1}, Si-O and C-O 1080, 1110 cm^{-1}. NMR δ 4.59 (sept., 1H, J = 2.8 Hz), 3.68 (q, 2H, J = 7 Hz), 1.19 (t, 3H, J = 7 Hz), 0.19 (d, 6H, J = 2.8 Hz). Mass spectrum: Parent m/e = 104 (44%), P-1 m/e = 103 (100%), P-15 m/e = 89 (72%), P-29 m/e = 75 (81%).

Photolysis of dodecamethylcyclohexasilane with ethanol-O-d_1 was carried out as above. Ethoxydimethylsilane-Si-d_1 was obtained in 84% yield. It had the following spectral properties: IR Si-D 1535 cm^{-1}, Si-O and C-O 1080, 1110 cm^{-1}. NMR δ 3.68 (q, 2H, J = 7 Hz), 1.19 (t, 3H, J = 7 Hz), 0.19 (s, 6H). Mass spectrum: Parent m/e = 105 (3.3%), P-2 m/e = 103 (54%), P-15 m/e = 90 (100%).

Photolysis of dodecamethylcyclohexasilane with t-butanol was carried out as above. t-Butoxydimethylsilane[9] was obtained in 85% yield. It had the following spectral properties. IR Si-H 2110 cm^{-1}, Si-O and C-O

1020 and 1045 cm^{-1}. NMR δ 4.72 (sept., 1H, J = 2.8 Hz), 1.26 (s, 9H), 0.16 (d, 6H, J = 2.8 Hz). Mass spectrum: Parent-1 m/e = 131 (0.2%), P-15 m/e = 117 (58%), P-57 m/e = 75 (100%).

Photolysis of dodecamethylcyclohexasilane with methanol was carried out as above except that THF was used in the place of ether as solvent. Methoxydimethylsilane[7] was obtained in 89% yield. It had the following spectral properties: IR Si-H 2120 cm^{-1}, Si-O and C-O broad 1095 cm^{-1}. NMR δ 4.57 (sept., 1H, J = 2.8 Hz), 3.45 (s, 3H), 0.19 (d, 6H, J = 2.8 Hz).

Photolysis of octamethyl-2,3-diphenyltetrasilane with t-butanol.

A mixture of ocatmethyl-2,3-diphenyltetrasilane (42.5 mg, 0.11 mmol) and t-butanol (122 mg, 1.65 mmol) was dissolved in ether (1.11 g, 15 mmol) in a quartz NMR tube.　　　This solution was photolyzed as above. GLPC analysis of the resulting pale yellow solution on a 1/4" x 12' 20% SE-30 on Chromosorb W 60/80 mesh column indicated a 77% yield of t-butoxymethylphenylsilane. It had the following spectral properties. IR Si-H 2130 cm^{-1}, Si-O and C-O 1020 and 1040 cm^{-1}. UV (cyclohexane) λ_{sh} 2470 Å (ϵ 397), λ_{max} 2530 (490), λ_{max} 2590 (600), λ_{max} 2640 (588), λ_{max} 2700 (441), λ_{sh} 2750 (206). NMR δ 7.62-7.45 (m, 2H), 7.39-7.25 (m, 3H), 5.12 (q, 1H, J = 2.8 Hz), 1.28 (s, 9H), 0.40 (d, 3H, J = 2.8 Hz). Mass spectrum: Parent m/e = 194 (16.5%), calcd. $C_{11}H_{18}OSi$ 194.113, found 194.115; P-15 m/e = 179 (75%); P-57 m/e = 137 (100%).

Acknowledgements

References

1. P.S. Skell and E.J. Goldstein, J. Am. Chem. Soc., 86 (1964) 1442.

2. H. Sakurai and M. Murakami, J. Am. Chem. Soc., 94 (1972) 5080.

3. W.H. Atwell and D.R. Weyenberg, J. Am. Chem. Soc., 90 (1968) 3438.

4. M. Ishikawa and M. Kumada, J. Organometal. Chem., 42 (1972) 325.

5. H.S.D. Soysa. H. Okinoshima, and W.P. Weber, J. Organometal. Chem., 133 (1977) C17.

6. H. Okinoshima and W.P. Weber, J. Organometal. Chem., 150 (1978) C25.

7. R. Okawara and M. Sakiyama, Bull. Soc. Chem., Japan, 29 (1956) 236.

8. M.E. Childs and W.P. Weber, J. Organometal. Chem., 86 (1975) 169.

9. J. Hetflejs. F. Mares, and V. Chvalovsky, Coll. Czech. Chem. Comm., 31 (1966) 586.

10. M. Ishikawa, M. Ishiguro, and M. Kumada, J. Organometal. Chem., 49 (1971) C71.

11. H. Okinoshima and W.P. Weber, J. Organometal. Chem., 155 (1978) 165.

12. J.L. Margrave, K.G. Sharp, and P.W. Wilson, Inorg. Nucl. Chem. Lett., 5 (1969) 995.

13. J.L. Margrave, K.G. Sharp, and P.W. Wilson, J. Am. Chem. Soc., 92 (1970) 1530.

14. A.I. Meyers, D.L. Temple, D. Haidukewych, and E.D. Mihelich, J. Org. Chem., 39 (1974) 2787.

15. K.A. Andrianov, T.K. Dzhashiashvili, V.V. Astakhim, and G.N. Shumakova, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 2162.

16. S.W. Jarvie and D. Lewis, J. Chem. Soc., (1963) 4758.

17. Merck, Sharp, and Dohme of Canada.

18. M. Laguerre, J. Dunogues, and R. Calas, J. Chem. Soc., Chem. Comm., (1978) 272.

19. R. West, Annals New York Academy of Sciences, 239 (1974) 262.

20. Petrach Systems.

Mechanism of the Reactions of Dimethylsilylene with Oxetanes

Tai-Yin Yang Gu and William P. Weber[*]

Department of Chemistry

University of Southern California

Los Angeles, California 90007

Abstract: Dimethylsilylene reacts with oxetane to give high yields of allyloxydimethylsilane and 2,2-dimethyl-1-oxa-2-silacyclopentane. These products result from decomposition of an initial 1,2-zwitterionic intermediate which is formed by coordination of the electrophilic dimethylsilylene with the oxygen of oxetane. Similar results have been obtained from the reactions of dimethylsilylene with 2-methyloxetane, 2,2-dimethyloxetane, and 3,3-dimethyloxetane.

We should like to report a novel insertion reaction of dimethylsilylene into the strained carbon-oxygen single bonds of oxetanes.[1] For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[2] in oxetane solvent at 0°C yields allyloxydimethylsilane[3] (I) (38%) and 2,2-dimethyl-1-oxa-2-silacyclopentane[4] (II) (41%). The yields reported are based on the generation of two dimethylsilylenes from each dodecamethyl-cyclohexasilane.[2]

$$[(CH_3)_2Si:] + \begin{array}{c}\square_O\end{array} \longrightarrow \diagup\diagdown O\text{-Si}(CH_3)_2 + \begin{array}{c}\bigcirc\end{array}Si(CH_3)_2$$

I   II
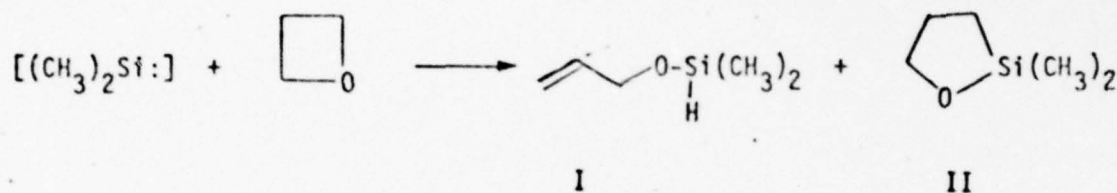
It should be noted that in control experiments no reaction of dimethyl-silylene with unstrained aliphatic ethers such as tetrahydrofuran or diethyl ether was observed.[5] The reaction of dimethylsilylene with oxetane to yield II must be quite exothermic (at least 100 kcal/mol) on the basis of thermochemical bond additivity. Thus, the reaction involves breaking a carbon-oxygen single bond (85.5 kcal/mol); formation of new silicon-carbon (76 kcal/mol) and silicon-oxygen (106 kcal/mol) single bonds;[6] and release of the oxetane strain energy ($\doteqdot$ 25 kcal/mol).[7] This calculation is incomplete due to the lack of knowledge concerning the probably small strain energy of II, which may result from constraint of a Si-O-C bond in a five membered heterocycle. The facile polymerization of II may reflect this strain energy.[8]

If II is formed by direct insertion of dimethylsilylene into a carbon-oxygen single bond of oxetane in a single step, one might assume

that II would be formed in a vibrationally excited ground state. This excess vibrational energy could be lost by collisional deactivation with solvent or by undergoing a retro-hydrosilation reaction to yield I.[9]
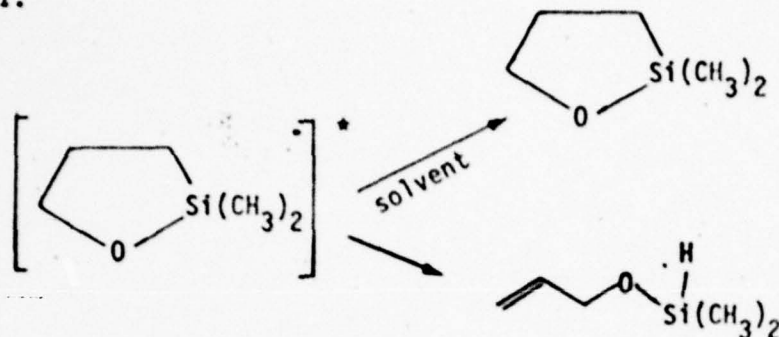
To test this hypothesis, the photolysis of dodecamethylcyclohexasilane in oxetane solvent was carried out at -98°C in a quartz Dewar. Under these conditions, we expected the ratio of I:II which is approximately 1:1 at 0° to shift in favor of II. However, under these conditions, the only product formed is I.

This led us to propose the following alternative hypothesis. Initial electrophilic attack by dimethylsilylene on a lone pair of electrons of the oxygen of the oxetane yields a zwitterionic intermediate (III) which can react further by two pathways. The first involves intra-molecular proton abstraction from C-3 of the oxetane ring by the negatively charged silicon with simultaneous fragmentation to yield I. A unique low energy vibrational puckering mode of the oxetane ring exists.[10] If a similar vibrational mode exists for the zwitterionic intermediate, it may permit the facile attainment of a non-planar puckered conformation which will bring a hydrogen atom on C-3 and the negatively charged silicon center into close proximity. This would favor this reaction pathway.

III
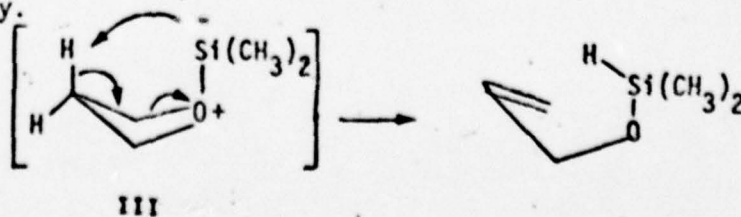
The second pathway involves heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate to yield a carbonium ion - silyl anion, a 1,5-zwitterion (IV), which combines by cyclization to yield II. The fact that at -98°C only I is formed indicates that the second pathway has a higher energy of activation than the first.

$$\text{III} \longrightarrow \text{IV} \longrightarrow$$
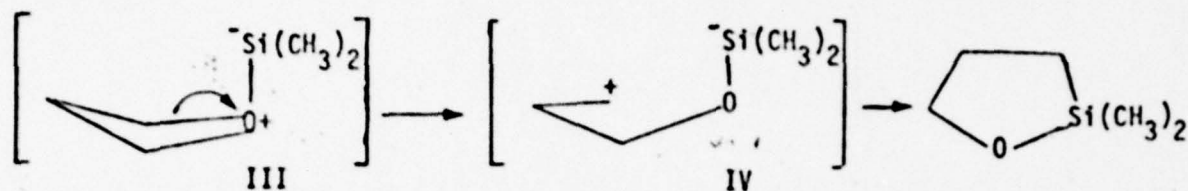
Additional support for this proposal comes from the following three experiments. Reaction of dimethylsilylene with 3,3-dimethyloxetane yields only 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (V) (90%).[11,12] Reaction of dimethylsilylene with 2,2-dimethyloxetane yields only 2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane (VI) (26%), 3-methyl-2-butenyloxydimethylsilane (VII) (44%)[3] and 3-methyl-3-butenyloxydimethyl-silane (VIII) (13%). The regiospecific formation of VI is expected since heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate is expected to lead to a tertiary carbonium ion in preference to a primary one. The formation of VII in preference to VIII is favored by the greater stability of the more substituted alkene product and by the more facile abstraction of a proton from a 2° carbon compared to a 1° one.
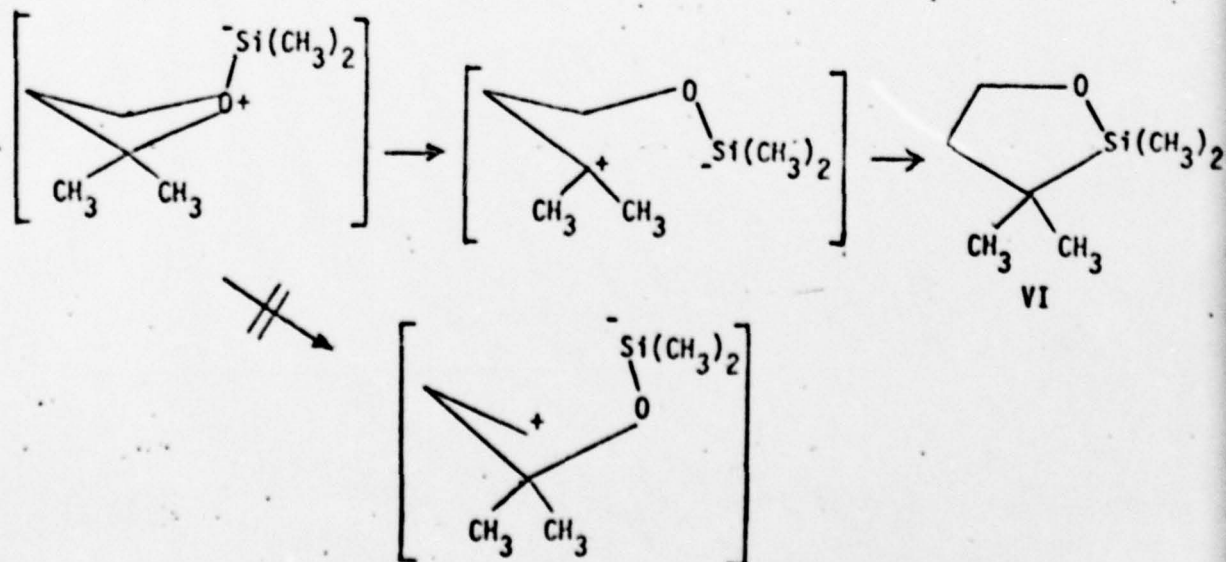
On the other hand, reaction of dimethylsilylene with 2-methyloxetane yields 2,2,3-trimethyl-1-oxa-2-silacyclopentane (IX) (29%), E-2-butenyloxydimethylsilane (X) (26%), Z-2-butenyloxydimethylsilane (XI) (22%) 1-methylallyloxydimethylsilane (XII) (1%), and 3-butenyloxydimethylsilane (XIII) (2%).[3] These latter two minor products were only identified by comparison of their GLPC retention times with authentic samples.

The regioselective formation of IX is expected since heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate is expected to lead to a secondary carbonium ion in preference to a primary one. The formation of IX was confirmed by independent synthesis of the other possible isomer, 2,2,5-trimethyl-1-oxa-2-silacyclopentane (XIV)[13] by an intramolecular hydrosilation reaction of 1-methylallyloxydimethylsilane catalyzed by chloroplatinic acid.[3]
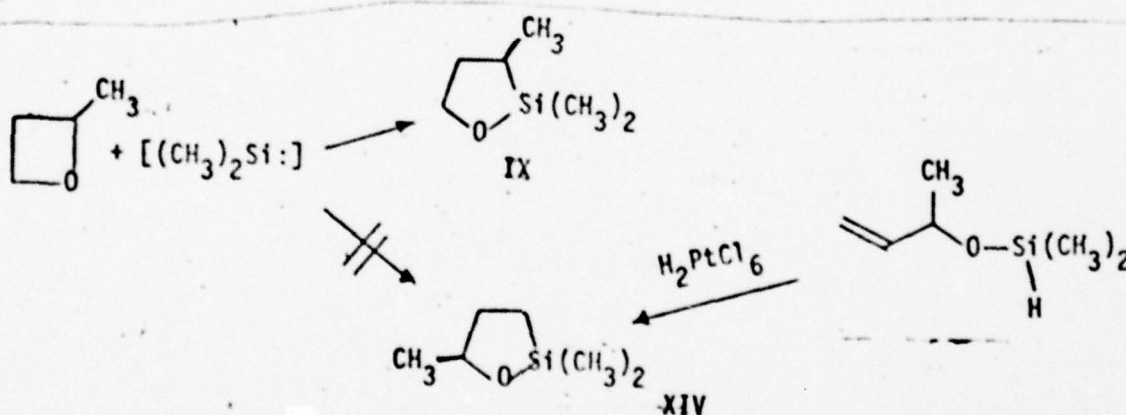
The predominant formation of X and XI rather than XII may result from preferential fragmentation of the 1,2-zwitterionic intermediate to form the more stable alkenes. The relative ease of proton abstraction from a secondary carbon compared to a primary carbon may control the relative amounts of XIII and XI formed.
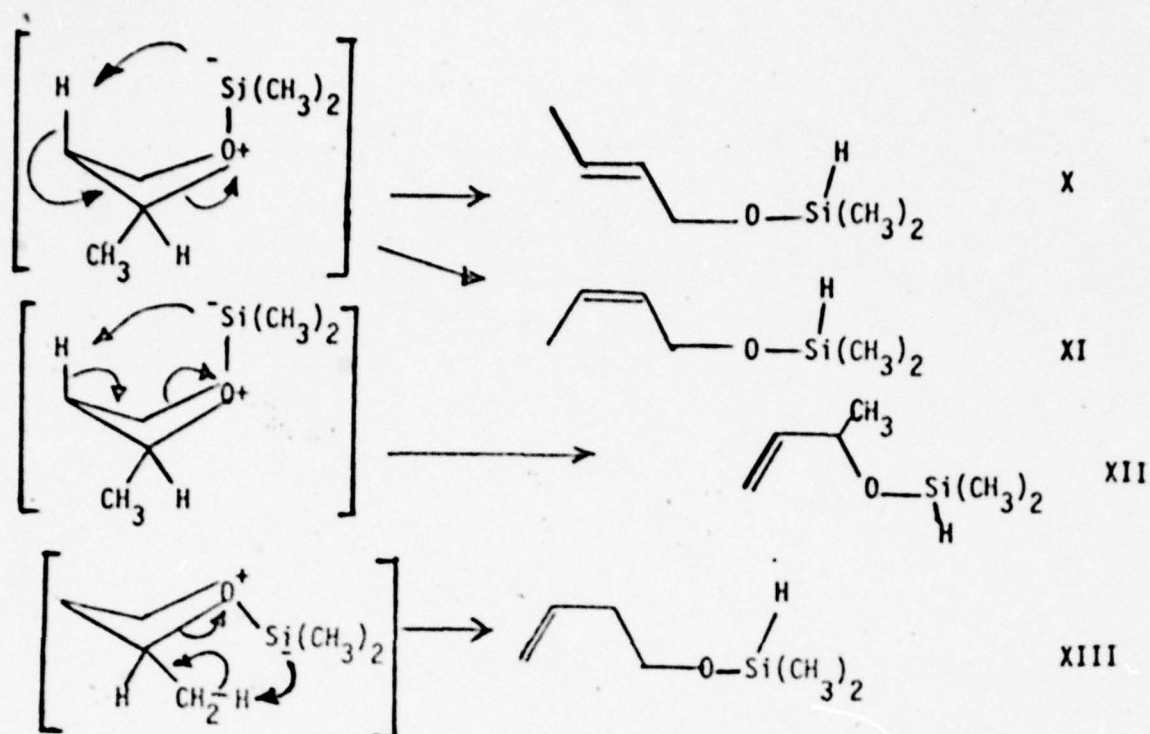
Based on these result we believe that the mechanism of reaction of dimethylsilylene with oxetanes involves initial electrophilic attack by dimethylsilylene on an oxygen lone pair of electrons to yield a 1,2-zwitterionic intermediate which further decomposes to yield a variety of products. These results should encourage caution in the interpretation of experiments involving dimethylsilylene carried out in "inert" ether solvents. Thus while dimethylsilylene does not react with unstrained aliphatic ethers to yield products, it may well form a complex with them. Such a zwitterionic complex might be capable of delivering dimethylsilylene to various substrates. The reactivity of dimethylsilylene may well be influenced by such solvation. This question is under active investigation.

Experimental

Ir spectra were determined as CCl_4 solutions on a Perkin-Elmer 281 spectrometer. Nmr spectra were recorded on a Varian XL-100 spectrometer using 5% solutions in $CDCl_3$ with an internal standard of chloroform. Mass spectra were determined on a duPont 21-492 at an ionizing voltage of 70 eV. Samples of all compounds for spectra analysis were purified by preparative vapor phase chromatography on a Hewlett Packard F&M 700. Yields of products were determined by GLPC with cyclooctane added as an internal standard. Yields are based on two moles of dimethylsilylene per mole of dodecamethylcyclohexasilane.

Many of the starting materials and products are known compounds. They had physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

<u>Reaction of dimethylsilylene with oxetane</u>. A solution of dodecamethyl-cyclohexasilane[14,15] (105 mg, 0.3 mmol) in oxetane[16] (1.16 g, 20 mmol) was placed in a quartz nmr tube. The solution was photolyzed with a 450 W medium pressure Hanovia Hg lamp for 90 min at 5°C in an ice/water bath. GLPC analysis of the resulting colorless solution on a 1/4" x 12' 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of 2,2-dimethyl-1-oxa-2-silacyclopentane[4] (41%) and allyloxydimethylsilane[3] (38%).

<u>2,2-Dimethyl-1-oxa-2-silacyclopentane</u> had the following spectral properties. Nmr δ 3.82 (t, 2H, J = 6 Hz), 1.85 (tt, 2H, J = 7.5 and 6 Hz), 0.72 (t, 2H, J = 7.5 Hz), 0.18 (s, 6H). Ir Si-O and C-O broad 1050, and 1085 cm^{-1}. Mass spectrum: Parent m/e = 116 (13%), P-1 m/e = 115 (1.7%), P-15 m/e = 101 (100%), P-17 m/e = 79 (16.9%), P-28 m/e = 88 (22.4%).

<u>Allyloxydimethylsilane</u> has the following spectral properties.

Nmr δ 5.93 (ddt, 1H, J = 17.1, 10.2, and 4.8 Hz), 5.23 (dq, 1H, J = 17.1 and 1.7 Hz), 5.09 (dq, 1H, J = 10.2 and 1.7 Hz), 4.62 (sept, 1H, J = 2.8 Hz), 4.16 (ddd, 2H, J = 4.8, 1.7 and 1.7 Hz), 0.21 (d, 6H, J = 2.8 Hz). Ir Si-H 2110 cm^{-1}; C=C 1650 cm^{-1}, Si-O and C-O 1030,1080 cm^{-1}. Mass spectrum: Parent m/e = 116 (4.6%), P-1 m/e = 115 (22%), P-15 m/e = 101 (79.7%), P-17 m/e = 99 (59%), P-31 m/e = 85 (15.6%), m/e = 75 (100%).

<u>Reaction of dimethylsilylene with 3,3-dimethyloxetane.</u>   A solution of dodecamethylcyclohexasilane in 3,3-dimethyloxatene[16] was prepared and photolyzed as above to yield 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (90%).[11,12] It had the following spectral properties: Nmr δ 3.49 (s, 2H), 1.03 (s, 6H), 0.66 (s, 2H),0.21 (s, 6H).   Ir Si-O 1020 cm^{-1}.   Mass spectrum Parent m/e = 144 (14%), calcd. $C_7H_{16}OSi$ 144.097; found 144.099;   P-15 m/e = 129 (13%), m/e = 99 (33%), m/e = 89 (100%), m/e 88 (54%).

<u>Reaction of dimethylsilylene with 2-methyloxetane.</u> A mixture of dodecamethylcyclohexasilane (90 mg, 0.26 mmol) and 2-methyloxetane[16] (360 mg, 5 mmol) in ether (630 mg, 8.5 mmol) was placed in a quartz nmr tube. The solution was photolyzed as above and the resulting colorless solution was analyzed by GLPC on a 1/4" x 28' 20% SE-30 on Chromosorb W 60/80 mesh column. E-2-butenyloxydimethylsilane (26%) Z-2-butenyloxy-dimethylsilane (22%) and 2,2,3-trimethyl-1-oxa-2-silacyclopentane (29%) were isolated.

<u>E-2-Butenyloxydimethylsilane</u> had the following spectral properties. Nmr δ 5.71 - 5.56 (m, 2H), 4.61 (sept, 1H, J = 2.8 Hz), 4.09 (d, 2H, J = 3.9 Hz), 1.68 (d, 3H, J = 4.7 Hz), 0.20 (d, 6H, J = 2.8 Hz). Ir Si-H 2115 cm^{-1}; Si-O and C-O 1080 and 1030 cm^{-1}. Mass spectrum: Parent m/e = 130 (15.1%), calcd. $C_6H_{14}OSi$ 130.081; found 130.081; P-1 m/e = 129 (6.2%), P-15 m/e = 115 (74.2%), P-17 m/e = 113 (5.9%),

m/e = 85 (17.7%), m/e = 75 (100%).

$\underline{Z}$-2-Butenyloxydimethylsilane has the following spectral properties.
Nmr δ 5.71 - 5.49 (m, 2H), 4.62 (sept, 1H, J = 2.8 Hz), 4.22 (d, 2H,
J = 4.7 Hz), 1.70 - 1.60 (m, 3H), 0.21 (d, 6H, J = 2.8 Hz). Ir Si-H
2120 cm^{-1} Si-O and C-O broad 1055 cm^{-1}. Mass spectrum: m/e = 130 (20%),
calcd. $C_6H_{14}OSi$ 130.081; found 130.081. P-1 m/e = 129 (15%), P=15
m/e = 115 (60%), m/e = 85 (16%), m/e = 75 (100%).

2,2,3-Trimethyl-1-oxa-2-silacyclopentane has the following spectral
properties. Nmr δ 3.84 - 3.44 (m, 2H), 1.84-1.59 and 1.52-1.24 (m and m, 1H and
1H, C-CH$_2$-C), 0.94 (d, 3H, J = 6Hz), 0.85-0.65 (m, 1H), 0.066 and 0.05 (s and s
3H and 3H, $Si(CH_3)_2$). Ir Si-O and C-O broad 1035 and 1015 cm^{-1}. Mass
spectrum: Parent m/e = 130 (20%), calcd. $C_6H_{14}OSi$ 130.081; found 130.081.
P-15 m/e = 115 (100%), m/e = 89 (27.6%), m/e = 88 (40%); m/e =87 (12.1%),
and m/e = 75 (35.2%).

1-Methylallyloxydimethylsilane was prepared by reaction of 3-buten-2-ol
with chlorodimethylsilane in the presence of N,N-dimethylaniline. It
had the following spectral properties. Nmr δ 5.83 (ddd, 1H, J = 17.1,
10.3, and 5.6 Hz), 5.14 (dt, 1H, J = 17.1 and 1.5 Hz), 5.00 (dt, 1H,
J = 10.3 and 1.5 Hz), 4.63 (sept, 1H, J = 2.9 Hz), 4.26 (dq, 1H, J =
5.6 and 6.3 Hz), 1.23 (d, 3H, J = 6.3 Hz), 0.19 (d, 3H, J = 2.9 Hz),
0.18 (d, 3H, J = 2.9 Hz). Ir Si-H 2110 cm^{-1}; C=C 1640 cm^{-1}, Si-O and
C-O broad 1070 and 1020 cm^{-1}. 1-Methylallyloxydimethylsilane undergoes
an intramolecular hydrosilation reaction catalyzed by chloroplatinic acid
to yield 2,2,5-trimethyl-1-oxa-2-silacyclopentane. The procedure used
was modeled after that of Mironov.[2] A mixture of 150 mg of 1-methyl-
allyloxydimethylsilane and 6 μl of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in
isopropyl alcohol was heated to boiling and then over a period of 2 h
the main portion (3 g) of the 1-methylallyloxydimethylsilane was added.
After cooling to room temperature, the reaction mixture was checked

by ir to observe complete disappearance of Si-H absorption. 2,2,5-Trimethyl-1-oxa-2-silacyclopentane was then collected from a simple bulb to bulb distillation. It had the following spectral properties. Nmr δ 4.02 - 3.90 (m, 1H), 2.03 - 1.91 and 1.44 - 1.31 (m and m, 1H and 1H, OCH$_2$C), 1.19 (d, 3H, J = 6 Hz), 0.89 - 0.63 (m, 2H), 0.16 (s, 6H). Ir Si-O and C-O 1045 and 1010 cm^{-1}. Mass spectrum: Parent m/e = 130 (0.5%), P-1 m/e = 129 (1.7%), calcd. C$_6$H$_{13}$OSi 129.074; found 129.074; P-15 m/e = 115 (100%), P-28 m/e = 120 (30.5%), P-29 m/e = 101 (7.4%), m/e = 87 (30.9%), m/e = 75 (17.5%).

E-2-butenyloxydimethylsilane was prepared independently by photolysis of dodecamethylcyclohexasilane with the commercial E-2-buten-1-ol in ether. This reaction involves insertion of dimethylsilylene into the O-H single bond.[19] 3-Butenyloxydimethylsilane was prepared from 3-buten-1-ol. By comparison of GC retention times, 1-methylallyloxydimethylsilane (1%) and 3-butenyloxydimethylsilane (2%) were found in the photolysis of dodecamethylcyclohexasilane in 2-methyloxetane.

2,2-Dimethyloxetane was prepared from 4-bromo-2-methyl-2-butanol[17] and tributylmethoxytin[18] following literature methods [17,18] and was purified by preparative GLPC. Nmr δ 4.00 (t, 2H, J = 8 Hz), 2.05 (t, 2H, J = 8 Hz), 1.00 (s, 6H).

Reaction of dimethylsilylene with 2,2-dimethyloxetane. A solution of dodecamethylcyclohexasilane in 2,2-dimethyloxatane was prepared and was photolyzed as above. Analysis of the resulting colorless solution by GLPC on a 1/4" x 28' 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of 3-methyl-3-butenyloxydimethylsilane (13%),[3] 3-methyl-2-butenyloxydimethylsilane (44%), and 2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane (26%). They had the following spectral properties. 3-Methyl-3-butenyloxydimethylsilane:[3] Nmr δ 4.76 (br.s, 1H), 4.71 (br.s, 1H), 4.60 (sept, 1H, J = 2.9 Hz), 3.72 (t, 2H, J = 7.0 Hz),

2.25 (t, 2H, J = 7.0 Hz), 1.73 (s, 3H), 0.19 (d, 6H, J = 2.9 Hz). Ir
Si-H 2110 cm^{-1}, C=C 1650 cm^{-1}, Si-O and C-O broad 1085 and 1060 cm^{-1}.
Mass spectrum: Parent m/e = 144 (2.5%), calcd. $C_7H_{16}OSi$ 144.097; found
144.098; P-1 m/e = 143 (1.7%), P-15 m/e = 129 (40.6%), m/e = 101 (11.1%),
m/e = 99 (7.6%), m/e = 89 (100%), m/e = 87 (10.5%), m/e = 75 (24.7%).

3-Methyl-2-butenyloxydimethylsilane: Nmr δ 5.33 (t, 1H, J = 6.6 Hz),
4.61 (sept, 1H, J = 2.8 Hz), 4.14 (d, 2H, J = 6.6 Hz), 1.72 (s,3H), 1.65 (s,3H),
0.20 (d, 6H, J = 2.8 Hz). Ir Si-H 2110 cm^{-1}, C=C 1670 cm^{-1}, Si=O and
C-O broad 1050 and 1025 cm^{-1}. Mass spectrum: Parent m/e = 144 (5.8%),
calcd. $C_7H_{16}OSi$ 144.097; found 144.099; P-1 m/e = 143 (0.9%), P-15
m/e = 129 (46.2%), m/e = 101 (9.4%), m/e = 89 (7.9%), m/e = 75 (100%).

2,2,3,3-Tetramethyl-1-oxa-2-silacyclopentane: Nmr δ 3.86 (t, 2H, J =
6.2 Hz), 1.61 (t, 2H, J = 6.2 Hz), 1.02 (s, 6H), 0.11 (s, 6H). Ir
Si-O and C-O 1030 and 1020 cm^{-1}. Mass spectrum: Parent m/e = 144 (23.7%),
calcd. $C_7H_{16}OSi$ 144.097; found 144.098. P-15 m/e = 129 (51.7%), m/e =
101 (9.4%), m/e = 99 (4%), m/e = 89 (24%), m/e = 88 (20%), m/e = 75 (100%).

References

1. For a recent review of silylene chemistry, see "Silylenes" by P.P. Gaspar in "Reactive Intermediates," vol. 1, edited by M. Jones, Jr. and R.A. Moss. Wiley-Interscience, New York, N.Y. 1978; p 229-277

2. M. Ishikawa and M. Kumada, J. Organometal. Chem., 42, 325 (1972).

3. V.F. Mironov, V.L. Kozlikov, and N.S. Nedotov, Zh. Obsh. Khim., 39, 937 (1969).

4. W.H. Knoth, Jr. and R.J. Lindsey, Jr., J. Am. Chem. Soc., 80, 4106 (1958).

5. Insertion of methoxymethylsilylene into a C-O single bond of 2,5-dimethylfuran has been previously reported, albeit in very low yield. M.E. Childs and W.P. Weber, J. Org. Chem., 41, 1799 (1976).

6. E.A.V. Ebsworth, Physical Basis of the Chemistry of the Group IV Elements, p. 45 in "Organometallic Compounds of the Group IV Elements," ed. A.G. MacDiarmid, Marcel Dekker, Inc., N.Y., N.Y., 1968.

7. H.K. Eigenmann, D.M. Golden, and S.W. Benson, J. Phys. Chem., 77, 1687 (1973).

8. A. Marchand, P. Gerval, M.H. Soulard, M. Massol, and J. Barrau, J. Organometal. Chem., 74, 209 (1974).

9. Synthesis and Reaction of the Silicon-Carbon Bond, C. Eaborn and R.W. Bott, pp. 213-313, in "Organometallic Compounds of the Group IV Elements Part I, ed. A.G. MacDiarmid, Marcel Dekker, Inc., N.Y., N.Y., 1968.

10. S.I. Chan, J. Zinn, and W.D. Gwinn, J. Chem. Phys., 34, 1319 (1961).

11. E.J.P. Fear, J. Thrower, and I.M. White, Chem. Ind. (London), 1877, (1961).

12. M.A.H. Hewins and I.M. White, Sci. Tech. Aerosp. Rep., 6, 1838 (1968); Chem. Abstr., 71, 102318t (1969).

13. G. Manuel, P. Mazerolles, and J.C. Florence, J. Organometal. Chem., 30, 5 (1971).

14. R. West, Annals. New York Academy of Science, 239, 262 (1974).

15. M. Laguerre, J. Dungues, and R. Calas, J. Chem. Soc. Chem. Commun., 272 (1978).

16. Aldrich Chemical Company.

17. B. Delmond, J.C. Pommier, and J. Valade, J. Organometal. Chem., 47, 337 (1973).

18. D.L. Alleston and A.G. Davies, J. Chem. Soc., 2050 (1962).

19. T.Y. Yang Gu and W.P. Weber, J. Organometal. Chem., in press (1979).

MASS SPECTROMETRY OF ARYL SUBSTITUTED DI- AND TRISILOXANES

Robert E. Swaim and William P. Weber*

Department of Chemistry
University of Southern California
Los Angeles, California 90007

Heinz G. Boettger, Margaret Evans, and Frank Bockhoff

Jet Propulsion Laboratory
Pasadena, California 91103

Abstract:

The mass spectra of arylpentamethyldisiloxanes, sym-diaryltetramethyl-disiloxanes, and 1,5-diaryl-1,1,3,3,5,5-hexamethyltrisiloxanes are discussed.

Disiloxanes are the simplest organosilicon compounds which process the silicon-oxygen-silicon functionality. Since silicon-oxygen-silicon bonds form the backbone of silicone polymers, disiloxanes serve as useful volatile models for these important polymers. While considerable work has been done on the mass spectral fragmentation patterns of trimethylsilyl ether derivatives of alcohols,[1-5] very little work has been done on the mass spectra of disiloxanes.[6,7] This is unfortunate because it is well known that the properties of the Si-O-Si functional group[8-10] are quite different from those of the Si-O-C functional group.

In this paper we will discuss the mass spectra of several types of aryl substituted disiloxanes and trisiloxanes.

The mass spectrum of phenylpentamethyldisiloxane (I) is dominated by siliconium ions. The parent ion is quite weak, probably because fragmentation of a methyl group from the quarternary silyl center to form the M-15 ion is such a favorable process.[11-13] The stability of the M-15 siliconium ion is reflected by the fact that it carries over 60% of the total ion current. At least three other important siliconium ions are formed by fragmentation and rearrangement of the M-15 ion.

A major process involves loss of methane from the M-15 ion. The observation of a metastable peak at m/e = 177-179 [calc. m/e = $(193)^2/209$ = 178.2] as well as the exact mass of the m/e = 193 ion determined by peak matching [calc. for $C_9H_{13}OSi_2$ 193.050; found 193.048] support this process. A possible mechanism for formation of the m/e = 193 ion involves initial intramolecular electrophilic attack by the remote siliconium

ion center of the M-15 ion at an _ortho_ position on the phenyl ring to yield a benzenonium ion which re-aromatizes by loss of a hydrogen from the benzenonium nucleus and a methyl group from a silyl center as methane. Examination of the mass spectrum of phenyl-d_5-pentamethyldisiloxane (II) indicates that this process may be more complicated. It certainly involves loss of a methyl group from silicon and most frequently loss of one deuterium from the phenyl-d_5 nucleus; however, some isotopic scrambling process occurs which leads to loss of methane rather than methane-d_1.

The two other major siliconium ions are the phenyldimethylsiliconium ion at m/e = 135 and the trimethylsiliconium ion at m/e = 73. The simplest explanation for their formation would be fragmentation of a Si-O bond of the parent ion. While we can not rule these process out, they are not supported by the observation of appropriate metastable peaks. On the other hand, metastable peaks are observed for formation of these siliconium ions by fragmentation of the M-15 ion. Thus the formation of the phenyldimethyl-siliconium ion from the M-15 ion by loss of dimethylsilanone $[(CH_3)_2Si=O]$ is supported by the observation of a metastable peak at m/e = 86.5 - 88 [calc. m/e = $(135)^2/209 = 87.2$], while the formation of the trimethylsili-conium ion at m/e = 73 from the M-15 ion by loss of phenylmethylsilanone $[\phi CH Si=O]$ is supported by the observation of a metastable peak at m/e = 25 - 26 [calc. m/e = $(73)^2/209 = 25.7$]. These processes are outlined in Scheme I.

Silanones are reactive intermediates possessing silicon-oxygen double bonds. They have been produced in pyrolysis reactions by interaction of intermediates possessing silicon-carbon double bonds with non-enolizable

ketones.[14-16] More recently, silanone intermediates have been genreated by photochemical deoxygenation reactions of silylenes with DMSO.[17]

$$[(CH_3)_2Si=CH_2] + \underset{\phi}{\overset{\phi}{\underset{|}{\overset{\parallel}{C}}}} \longrightarrow [\phi\overset{O-Si(CH_3)_2}{\underset{\phi}{\boxed{}}}] \longrightarrow \phi_2C=CH_2 + [(CH_3)_2Si=O]$$

$$[(CH_3)_2Si] + CH_3-\underset{\overset{|}{O}}{S}-CH_3 \longrightarrow [(CH_3)_2Si=O] + CH_3-S-CH_3$$
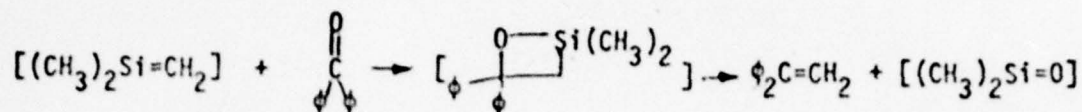
While there are many analogies between the high energy processes of pyrolysis-photolysis and mass spectrometry,[18] we believe that these observations are the first examples of the loss of silanones $[R_2Si=O]$ from siliconium ion in the gas phase in a mass spectrometer.

Finally, it should be noted that a series of doubly charged siliconium ions are of importance in the mass spectra of I. It has previously been observed that doubly charged siliconium ions are important in the mass spectrum of hexamethyldisiloxanes.[19] The doubly charged ion of highest mass is found at $m/e = 104.5$ which corresponds to the doubly charged M-15 ion. Loss of a methyl radical from the quarternary silyl center of this ion leads to a bis-siliconium ion at $m/e = 97$. The observation of an isotope peak of the appropriate intensity at $m/e = 97.5$ supports this assignment of the $m/e = 97$. The stability of this bis-siliconium ion is reflected by the fact that it carries almost 10% of the total ion current. The bis-siliconium ion of $m/e = 97$ undergoes further loss of methane. This process is supported by the observation of a metastable peak at $m/e = 81.5-82.5$ [calc. $m/e = (89)^2/97 = 81.7$]. A possible mechanism for formation of the $m/e = 89$ ion involves initial intramolecular eletrophilic attack by the remote siliconium ion center at an ortho position of the phenyl ring to yield a benzenonium ion which re-aromatizes

by loss of hydrogen from the benzenonium nucleus and a methyl group from a silyl center as methane. The mass spectrum of II supports this process since methane-d_1 is exclusively lost. These processes are outlined in Scheme II.

Similar fragmentation patterns supported by appropriate metastable peaks were observed for II and for p-tolylpentamethyldisiloxane (III) (see Table I for supporting data).

The second group of aryl substituted disiloxanes whose mass spectra we have examined is composed of: sym-tetramethyldiphenyldisiloxane (IV), sym-tetramethyldiphenyl-(2,4,6-2',4',6')-d_6-disiloxane (V), sym-tetramethyldiphenyl-d_{10}-disiloxane (VI), and sym-tetramethyldi-p-tolyldisiloxane (VII), 1,1,1,3-tetramethyl-3,3-diphenyldisiloxane (VIII) and 1,1,1-trimethyl-3,3,3-triphenyldisiloxane (IX).

The mass spectrum of sym-tetramethyldiphenyldisiloxane (IV) is dominated by siliconium ions. The parent ion is quite weak, probably due to the fact that fragmentation of a methyl group from a quarternary silyl center to form the M-15 siliconium ion is such a favored process. The stability of the M-15 ion is reflected by the fact that it carries 30% of the total ion current. On the other hand, loss of a phenyl group from the parent ion to form the M-77 ion at m/e = 209 is a much less favorable process. The M-15 undergoes further fragmentation and rearrangement to yield at least four other siliconium ions which are important in the mass spectrum of IV.

A major process involves loss of benzene from the M-15 ion. The observation of a metastable peak at m/e = 136 - 139 [calc. m/e = $(193)^2/271 = 137.5$] as well as the exact mass of the m/e = 193 ion

determined by peak matching [calc. for $C_9H_{13}OSi_2$ 193.050, found 193.052] support this process. The importance of this process is reflected in the fact that the m/e = 193 ion carries 15% of the total ion current. A possible mechanism for formation of the m/e = 193 ion involves initial intramolecular electrophilic attack by the remote siliconium ion center of the M-15 ion at an _ortho_ position of the distant phenyl ring to yield a benzenonium ion which re-aromatizes by loss of a hydrogen from the benzenonium nucleus and a phenyl group from a silyl center as benzene. This benzenonium ion can also re-aromatize by loss of hydrogen from the benzenonium nucleus and a methyl group from a silyl center as methane to yield the m/e = 255 siliconium ion. This process is supported by the observation of a metastable peak at m/e = 239 - 242 [calc. m/e = $(255)^2/271 = 239.9$]. However, the loss of methane is not favored since the m/e = 255 ion carries only approximately 1% of the ion current. Examination of the mass spectra of V and VI support these processes. Thus benzene-d_6 is lost in the case if VI. However, the hydrogen which is lost from the benzenonium ion nucleus apparently may not come specifically from the _ortho_ site of electrophilic attack. Thus V looses both benzene-d_4 and benzene-d_3 in this process. Isotopic scrambling of hydrogens and deuteriums in benzenonium ions formed by intramolecular electrophilic attack by siliconium ions centers on aryl groups has been previously reported.[20]

The M-15 ion also fragments by loss of dimethylsilanone [$(CH_3)_2Si=O$] to yield the diphenylmethylsiliconium ion at m/e = 197. This process is supported by the observation of a metastable peak at m/e = 143.2 - 143.4 [calc. m/e = $(197)^2/271 = 143.3$]. Finally, the M-15 ion fragments by loss

of phenylmethylsilanone [$\phi CH_3 Si=O$] to yield the phenyldimethylsiliconium ion at m/e = 135. A metastable peak for the analogous process was observed in the mass spectrum of V. However, no metastables were seen in the spectra of IV, VI, or VII. An alternative process for formation of the phenyldimethylsiliconium ion is simple fragmentation of an Si-O bond of the parent ion. This possibility is not supported by appropriate metastable peaks in the spectra of any of the sym-diaryltetramethyldisiloxanes studied. The stability of the phenyldimethylsiliconium ion is reflected by the fact that it carries almost 10% of the total ion current. These processes are outlined in Scheme III.

The M-15 ion is important in the mass spectra of both VIII and IX. In both spectra this ion carries about 25% of the total ion current. In both the loss of benzene from the M-15 is a very important process. Thus in the mass spectra of VII the loss of benzene from the M-15 ion is supported by the observation of a metastable peak at m/e = 136 - 138.5 [calc. m/e = $(193)^2/271$ = 137.5] as well as by the exact mass of the m/e = 193 ion determined by peak matching [calc. for $C_9H_{13}OSi_2$ 193.050; found 193.052]. The m/e = 193 ion carries greater then 13% of the total ion current. In the mass spectra of IX the loss benzene from the M-15 ion is supported by the observation of a metastable peak at m/e = 195 - 197 [calc. m/e = $(255)^2/333$ = 195.3] as well as by the exact mass of the m/e = 255 ion determined by peak matching [calc. for $C_{14}H_{15}OSi_2$ 255.066, found 255.068]. The m/e = 255 ion carries greater than 16% of the total ion current. This process is outlined in Scheme IV.

It should be noted that a series of doubly charged ions are of
importance in the mass spectra of diaryltetramethyldisiloxanes IV, V, VI,
VII and VIII. The doubly charged ion of highest mass in the spectra of
IV is found at m/e = 143 which corresponds to a doubly charged parent
ion. An isotope peak of appropriate intensity at m/e = 143.5 confirms
this assignment. Loss of a methyl radical from this doubly charged ion
leads to the m/e = 135.5 doubly charged siliconium ion. This ion may
also be formed by loss of an electron from the M-15 siliconium ion.
The doubly charged m/e = 135.5 ion further fragments by loss of methyl
radical probably from the uncharged silyl center to yield a bis-siliconium
ion of m/e = 128. An isotope peak of appropriate intensity at m/e = 128.5
supports this assignment. This bis-siliconium ion further fragments by
loss of benzene to yield the bis-siliconium ion of m/e = 89. A possible
mechanism for formation of the m/e = 89 doubly charged ion involves
initial intramolecular electrophilic attack by the remote siliconium ion
center on the distant phenyl ring to yield a benzenonium ion which
re-aromatizes by lost of a hydrogen from the benzenonium ion and a phenyl
group from a silyl center as benzene. The stability of the doubly charged ions
of m/e = 128 and m/e = 89 is reflected in the fact that they carry
respectively 3% and 5% of the total ion current. These processes are
outlined in Scheme V.

Similar fragmentation patterns supported by appropriate metastable
peaks were observed from diaryltetramethyldisiloxanes (IV, V, VI, VII and
VIII) and for 1,1,1-trimethyl-3,3,3-triphenyldisiloxane (IX) (See Table
II for supporting data).

We have examined the mass spectra of four 1,5-diaryl-1,1,3,3,5,5-
hexamethyltrisiloxanes: 1,1,3,3,5,5-hexamethyl-1,5-diphenyltrisiloxane (X),

1,1,3,3,5,5-hexamethyl-1,5-diphenyl-(2,4,6-2',4',6')-d_6-trisiloxane
(XI), 1,1,3,3,5,5-hexamethyl-1,5-diphenyl-d_{10}-trisiloxane (XII), and
1,1,3,3,5,5-hexamethyl-1,5-di-p-tolyltrisiloxane (XIII). The parent
ion is quite weak. Loss of a methyl radical from the parent ion leads
to the M-15 siliconium ion at m/e = 345, whose stability is reflected
in the fact that it carries 43% of the total ion current. By comparison
loss of a phenyl from the parent is a very unimportant process. The
M-15 ion undergoes further fragmentation and rearrangement to yield at
least three other important siliconium ions.

A major process involves loss of benzene from the M-15 ion to
yield a siliconium ion of m/e = 267 which carries 8% of the total ion
current. The observation of a metastable peak at m/e = 205 - 208
[calc. m/e = $(267)^2/345$ = 206.6] supports this process. A possible
mechanism for formation of this ion involves an intramolecular electro-
philic attack by a terminal siliconium ion center on a remote phenyl group
of the M-15 ion to yield a benzenonium ion which re-aromatizes by loss
of a hydrogen from the benzenonium nucleus and a phenyl group from
silicon. This process is also observed in the mass spectra of XI, XII,
and XIII. In the case of XII, the M-15 ion loses benzene-d_6 while in
the case of the M-15 ion XIII loses toluene. The mass spectrum of
XI is more complicated. The M-15 ion loses both benzene-d_3 and benzene-d_4.
Apparently, scrambling of hydrogen and deuterium occurs in the benzenonium
nucleus prior to loss of benzene.

The M-15 ion also rearranges and undergoes loss of tetramethyl-
cyclodisiloxane to yield the diphenylmethylsiliconium ion at m/e = 197,
which carries 6% of the total ion current. A metastable peak at m/e =

112 - 113 [calc. m/e = $(197)^2/345$ = 112.5] supports this process.
The loss of tetramethylcyclodisiloxane is of interest since it is unknown,
although it is a reasonable intermediate in the cyclo-oligomerization of
dimethylsilanone to yield hexamethylcyclotrisiloxane in the gas phase.[16,21]
In addition, it has previously been proposed to account for the mass
spectra of methyl siloxanes.[22] The M-15 ion also fragments with loss
of trimethylphenylcyclodisiloxane to yield the dimethylphenylsiliconium
ion at m/e = 135 which carries 12% of the total ion current.
A metastable peak at m/e = 52.5 - 53.0 [calc. m/e = $(135)^2/345$ = 52.8]
supports this process. Alternatively, the m/e = 135 siliconium ion
may be formed by fragmentation of a terminal Si-O bond of the parent
ion. While this possibility can not be eliminated, it is not supported
by the observation of appropriate metastable peaks. These processes are
outlined in Scheme VI.

The M-15 ion also loses a methyl radical to yield a doubly charged
siliconium ion of m/e = 165, which carries 7% of the ion current. An
isotope peak at m/e = 165.5 of appropriate intensity supports this
assignment. This doubly charged ion undergoes loss of benzene to yield
a doubly charged siliconium ion of m/e = 126, which carries 2% of the
ion current. This process is supported by the observation of an appropriate
metastable peak at m/e = 96 - 97 [calc. m/e = $(126)^2/165$ = 96.2]. A
possible mechanism for the formation of this ion involves an intramolecular
electrophilic attack by a siliconium on a remote phenyl group to yield
a benzenonium ion which re-aromatizes by loss of hydrogen from the
benzenonium nucleus and a phenyl group from a silyl center. These
processes are outlined in Scheme VII.

Experimental

IR spectra were determined as 10% solutions in CCl_4 on a Perkin-Elmer 281 spectrometer. They were calibrated versus known bands of a polystyrene film. UV spectra were run in spectro-quality cyclohexane on a Beckman Acta M spectrometer. NMR samples were run as 0.1 molar solution in acetone-d_6 with dichloromethane as an internal standard on a Varian X1-100-15 operating in the CW mode. All samples were purified by gas liquid phase chromatography (GLPC) on either a 36" x 0.25" 20% DCQF-1 on Chromosorb W 60/80 mesh or on a 36" x 0.25" 20% SE-30 on Chromosorb W 60/80 mesh column on a Hewlett-Packard F&M 700 chromatography. Low resolution mass spectra were determined at 70 eV by using an AEI MS-9 spectrometer at the Jet Propulsion Laboratory, Pasadena, California. High resolution mass spectra were run on a DuPont 21-492 at 70 eV ionizing voltage at the California Institute of Technology Analytical Laboratory, Pasadena, California.

Virtually all of the siloxanes studied are known compounds. They were prepared following literature methods. Their physical and spectral properties are in full agreement with literature values. In those cases where complete spectral information has not been previously reported, we have included this data.

Phenylpentamethyldisiloxane.[23,24] NMR δ 7.17 ppm (m, 5H), 0.07 (s, 6H), -0.016 (s, 9H). UV λ_{max} 272.3 nm (ϵ = 152), 267.9 (212), 266.2 (207), 261.4 (233), 255.5 (162), 249.0 (92), 221.2 (6373), 212.0 (9392). IR Si-CH_3 1252, Si-Ph 1155, and Si-O-Si 1050 cm^{-1}.

Phenyl-d_5-pentamethyldisiloxane was prepared by photochemical oxidation of phenyl-d_5-pentaethyldisilane with DMSO.[24] IR C-D 2275, Si-CH_3 1256, and Si-O-Si 1050 cm^{-1}. Mass spectral data: see Table I.

Phenyl-d_5-pentamethyldisilane was prepared as follows: to 0.43 g
(18.0 mmol) of Mg turnings in a flame-dried 100 ml three necked flask
equipped with a magnetic stirring bar, a reflux condenser, a gas inlet,
and a pressure equalizing addition funnel was added 3.0 g (18.0 mmol)
of bromobenzene-d_5[25] in 50 ml of THF dropwise over 15 minutes. The
mixture was stirred for three hours at r.t. Pentamethylchlorodisilane[26]
3.0 g (18.0 mmol) was added dropwise over 20 minutes. The reaction was
stirred at reflux for 18 h then allowed to cool to room temperature.
The magnesium salts were removed by filtration through Celite and the
filtrate was washed with a saturated solution of NH_4Cl. The organic
layer was concentrated by simple distillation. A sample of phenyl-d_5-
pentamethyldisilane was purified by GLPC on SE-30. Phenyl-d_5-penta-
methyldisilane: IR C-D 2260, C-D 2240, Si-Ph 1610, 1400, Si-$(CH_3)_3$ 1250.
Mass spectral: m/e = 213 M, 7.6%, 198, M-15, 8.2%, 140, ϕ-d_5-$\overset{+}{S}i(CH_3)_2$.

p-Tolylpentamethyldisiloxane:[24] UV 271.7 (198), 266.0 (251),
259.8 (209), 253.3 (162), 227.4 (8536), 2234 (10,563), 218.6 (9496).

sym-Tetramethyldiphenyldisiloxane. IV[24,27-29]

sym-Tetramethyldiphenyl-d_6-disiloxane (V) was prepared by reaction of
2,4,6-trideuteriophenylmagnesium chloride with 1,3-dichlorotetramethyl-
disiloxane[30,31] as follows: to 0.29 g (12.1 mmol) of Mg turnings in a
flame dried 50 ml three-necked flask equipped with a magnetic stirring
bar, a reflux condenser, a gas inlet, and an addition funnel, 1.44 g
(12.54 mmol) of chloro-2,4,6-trideuterobenzene[32] (73% d_3, 23% d_2, 46% d_1)[33]
in 25 ml of THF was added over 15 minutes. The reaction mixture was stirred
while refluxing for 12 h until all the magnesium was dissolved. The
solution was allowed to cool to room temperature before 0.80 g (6.0 mmol)
of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane[30] was added dropwise over
20 minutes. The reaction was refluxed for another 18 h. The solid

material was filtered from the cooled solution and the filtrate was extracted with Et_2O/H_2O . The organic extract was concentrated by simple distillation. A sample of V was purified by GLPC. It had the following spectral properties. IR C-D 2250, Si-CH$_3$ 1258, Si-Ph 1135, Si-O-Si 1054 cm^{-1}. Mass spectral data see Table II.

sym-Tetramethyldiphenyl-d$_{10}$-disiloxane. VI[34] Mass spectral data, Table II.

sym-Tetramethyl-di-p-tolyldisiloxane: VII[30,31,35] UV 287.5 (59), 270.9 (448), 265.1 (568), 258.5 (517), 254.0 (433), 228.5 (19,049), 223.0 (23,829), 219.8 (23,739), IR Si-CH$_3$ 1252, Si-Ar 1110, and Si-O-Si 1050 cm^{-1}. NMR δ 7.22 (m, 4H), 2.33 (s, 6H), 0.37 (s, 12H).

1,1,1,3-Tetramethyl-3,3-diphenyldisiloxane:[23,24] III UV 270.5 (404), 266.0 (510), 264.0 (536), 259.6 (555), 253.4 (411), 247.8 (278), 223 (15,818), 215 (17,400). IR Si-CH$_3$ 1255, Si-Ph 1115, and Si-O-Si 1060 cm^{-1}.

1,1,1-Trimethyl-3,3,3-triphenyldisiloxane IX[23,36,37]

1,1,3,3,5,5-Hexamethyl-1,5-diphenyltrisiloxane:[23,34] X UV 271.8 (475), 267.0 (653), 265.3 (655), 261.0 (741), 255.0 (584), 249.4 (431), 211.0 (26,601).

1,1,3,3,5,5-Hexamethyl-1,5-diphenyl-(2,4,6-2',4',6')-trisiloxane: XI was prepared by addition of 2,4,6-trideuteriophenylmagnesium chloride to 1,5-dichloro-1,1,3,3,5,5-hexamethyldisiloxane[30] as above. It had the following spectral properties. IR C-D 2245, Si-CH$_3$ 1260, Si-Ph 1135, Si-O 1080 and 1045 cm^{-1}. Mass spectral data, see Table III.

1,1,3,3,5,5-Hexamethyl-1,5-diphenyl-d$_{10}$-trisiloxane: XII was prepared by reaction of phenyl-d$_5$-magnesium bromide with 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane[30] as above. It had the following spectral properties IR C-D 2270, and 2240, Si-CH$_3$ 1258, Si-O 1080 and 1045 cm^{-1}. Mass spectral data, see Table III.

1,1,3,3,5,5-Hexamethyl-1,5-di-p-tolyltrisiloxane: XIII was prepared by reaction of p-tolylmagnesium bromide with 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisloxane[30,31] as above. It had the following spectral properties. UV 269.1 (427), 262.8 (538), 256.8 (485), 251.7 (414), 227 (24,040), 223.5 (28,186), 218 (26,867), 214 (25,085). IR Si-CH$_3$ 1258, Si-Ph 1110 and Si-O 1040 cm^{-1}. NMR δ 6.94 (m, 8H), 2.33 (s, 6H), 0.11 (s, 12H), 0.05 (s, 6H). For mass spectral data, see Table III.

1. J. Diekman, J.B. Thomson, and C. Djerassi, J. Org. Chem., 32 (1967) 3904.

2. J. Diekman, J.B. Thomson and C. Djerassi, J. Org. Chem., 33 (1968) 2271.

3. W.J. Richter and D.H. Hunnemann, Helv. Chim. Acta, 57 (1974) 1131.

4. D.C. DeJongh, T. Radford, J.D. Hribar, S. Hanessian, M. Bieber, G. Dawson, and C.C. Sweeley, J. Am. Chem. Soc., 91 (1969) 1728.

5. E. White and J.A. McCloskey, J. Org. Chem., 35 (1970) 4241.

6. V.Y. Orlov, Zhur. Obsh, Khim. 37 (1967) 2300.

7. J.E. Coutant and R.J. Robinson, Mass Spectrometry in Analysis of Silicones, editor A.L. Smith, J. Wiley & Sons, N.Y. (1974), p. 338-375.

8. For a review see: C. Eaborn, Organosilicon Compounds, Buttersworth Scientific Publication, London (1960), Chapter 8 and 9.

9. For a review see: Physical Basis of the Chemistry of the Group IV Elements by E.A.V. Ebsworth, in Organometallic Compounds of the Group IV Elements, Vol. I, Edited by A.G. MacDiamond, M. Dekker Inc., N.Y. (1968).

10. H. Okinoshima and W.P. Weber, J. Organometal. Chem., 150 (1978) C 25.

11. N.Y. Chernyak, R.A. Khmel'nitskii, T.V. D'yakova and V.M. Vdovin, Zhur. Obsh. Khim., 36 (1966) 89.

12. N.Y. Chernyak, R.A. Khmel'nitskii, T.V. D'yakova, V.M. Vdovin and T.N. Arkhipova, Zhur. Obsh. Khim., 36 (1966) 96.

13. T.H. Kinstle, P.J. Ihrig, and E.J. Goettert, J. Am. Chem. Soc., 97 (1970) 1780.

14. D.N. Roark and L.H. Sommer, J. Chem. Soc. Chem. Commun. (1973) 167.

15. T.J. Barton, E.A. Kline and P.M. Garvey, J. Am. Chem. Soc., $\underline{95}$ (1973) 3078.

16. C.M. Golino, R.D. Bush, D.N. Roark and L.H. Sommer, J. Organometal. Chem., $\underline{66}$ (1974) 29.

17. H.S.D. Soysa, H. Okinoshima and W.P. Weber, J. Organometal. Chem. $\underline{133}$ (1977) C17.

18. R.C. Dougherty, Topics in Current Chemistry, Vol. 45, Springer-Verlag, Berlin, Heidelberg, N.Y., 1974, pp. 93.

19. V.H. Dibeler, F.L. Mohler, and R.M. Reese, J. Chem. Phys., $\underline{21}$ (1953) 180.

20. W.P. Weber, A.K. Willard and H.G. Boettger, J. Org. Chem., $\underline{36}$ (1971) 1620.

21. L.E. Gusel'nikov, N.S. Nametkin, T. Kh. Islamov, A.A. Sobtsov, and V.M. Vdovin, Izv. Akad. Nauk. SSSR Ser. Khim, 84 (1971).

22. G.B. Tanny and L.E. St. Pierre, J. Phys. Chem., $\underline{75}$ (1971) 2430.

23. W.H. Daudt and J.F. Hyde, J. Am. Chem. Soc., $\underline{74}$ (1952) 386.

24. H. Okinoshima and W.P. Weber. J. Organomet. Chem., 149 (1978) 279.

25. Aldrich Chemical Company.

26. M. Kumada, M. Yamaguchi, Y. Yamamoto, J-I. Nakajima, and K. Shiina, J. Org. Chem., $\underline{21}$ (1957) 1264.

27. R.N. Lewis, J. Am. Chem. Soc., $\underline{70}$ (1948) 1115.

28. C. Burkhard and E.H. Winslow, J. Am. Chem. Soc., $\underline{72}$ (1950) 3276.

29. V. H. Kriegsman, Z. Anorg. Chem., $\underline{299}$ (1959) 78.

30. P. Patnode and D.F. Wilcock, J. Am. Chem. Soc., $\underline{68}$ (1946) 358.

31. H. Manami and S. Nishizaki, Japan J. Pure Chem., $\underline{79}$ (1958) 60.

32. J.M. Scarborough, U.S. Atomic Energy Comm. NAA-SR-2144 (1957) 11.

33. K. Bieman, "Mass Spectrometry Organic Chemical Applications", McGraw-Hill Book Company, Inc., New York, N.Y. (1962), pp. 223.

34. H.S.D. Soysa and W.P. Weber, J. Organometal. Chem., in press (1979).

35. J.C. Bonnet and E.Marechal, Bull. Soc. Chim. Fr. (1972) 3561.

36. R.E. Swaim, W.P. Weber, J. Am..Chem. Soc., in press (1979).

37. J. Homer, A.W. Jarvie, A. Holt and H.J. Hickton, J. Chem. Soc. (B), (1967) 67.

SCHEME I

*metastable observed
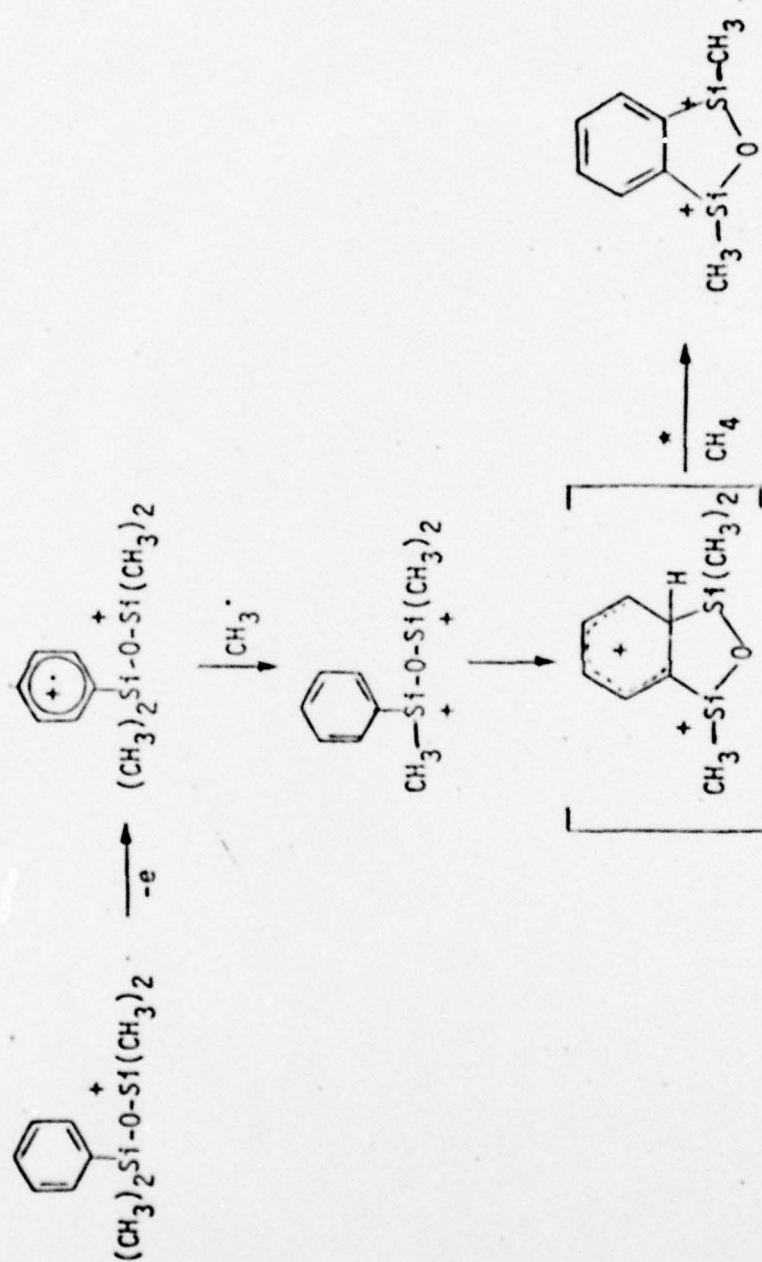
SCHEME II

*metastable observed
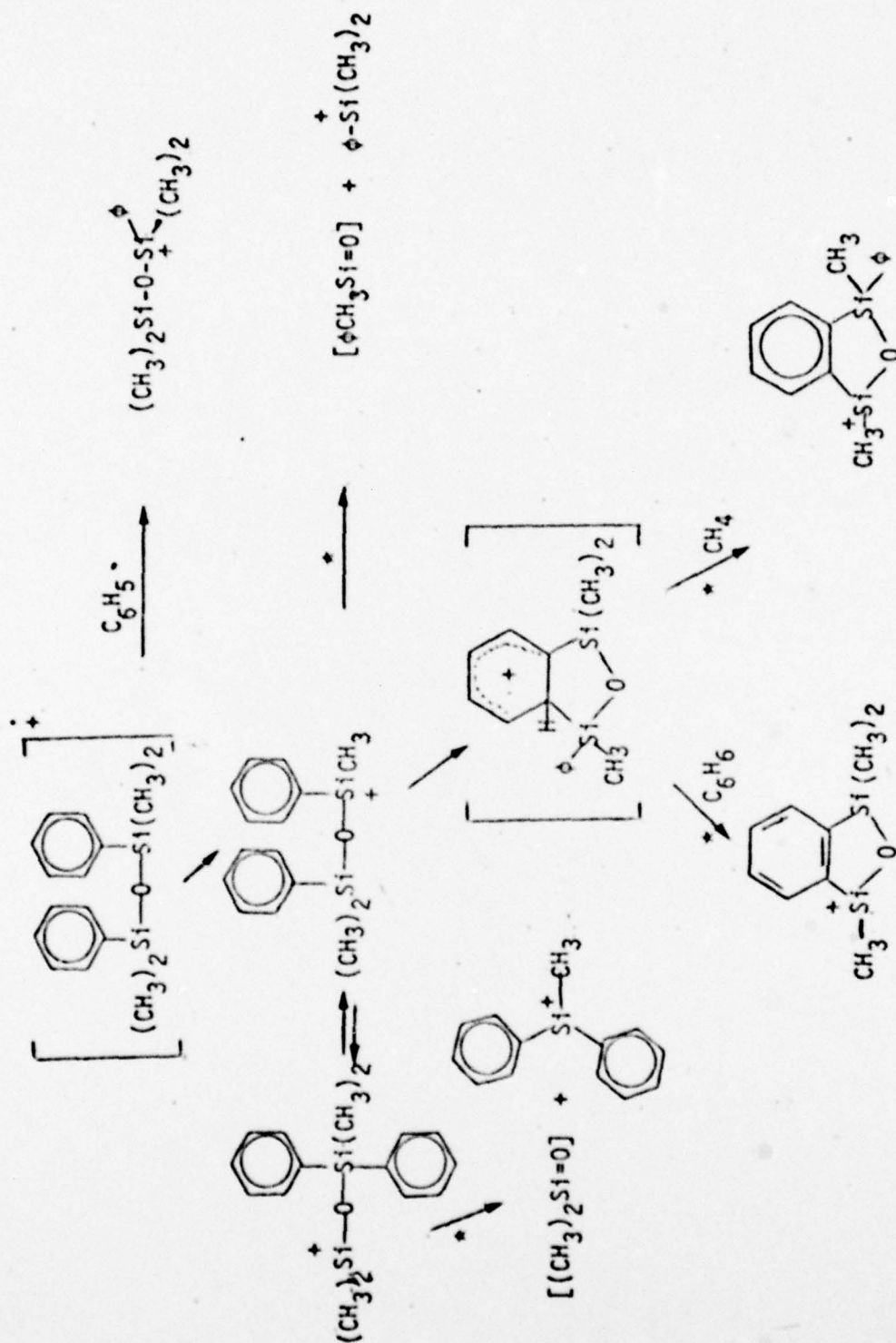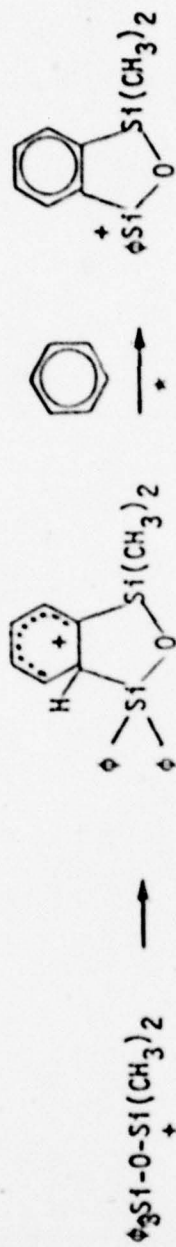
SCHEME III

*metastable observed
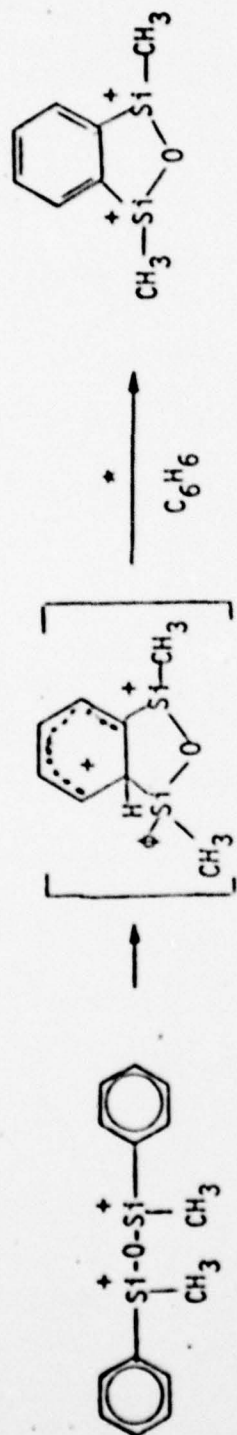
SCHEME IV

*metstable observed
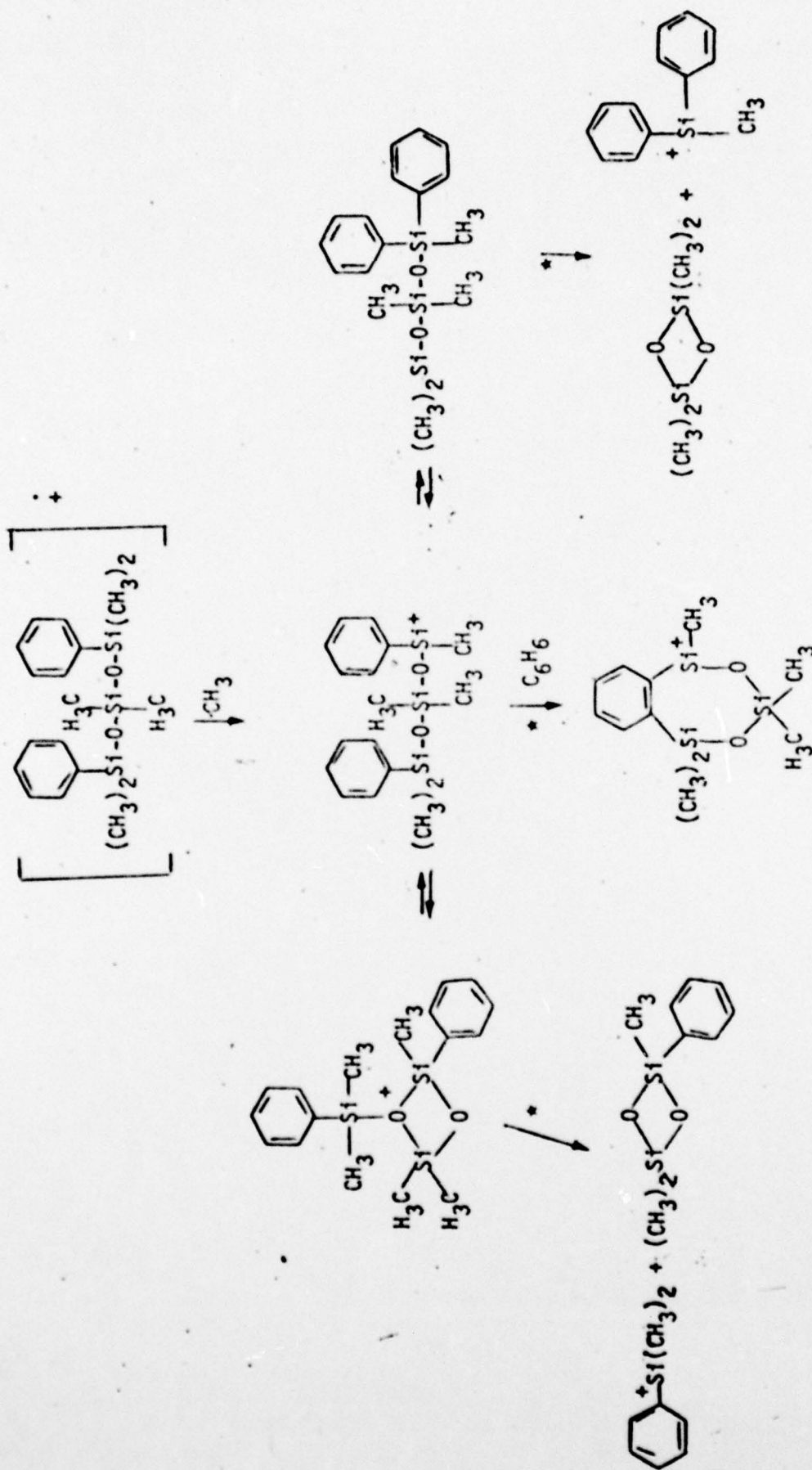
SCHEME V

*metastable observed

SCHEME VI

*metastable observed

$(CH_3)_2-Si-O-Si-O-Si^+$
CH_3 CH_3

$\xrightarrow{\quad *\quad}$
C_6H_6

$(CH_3)_2-Si$
Si^+-CH_3
Si
CH_2
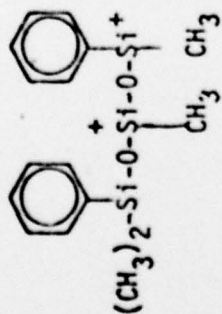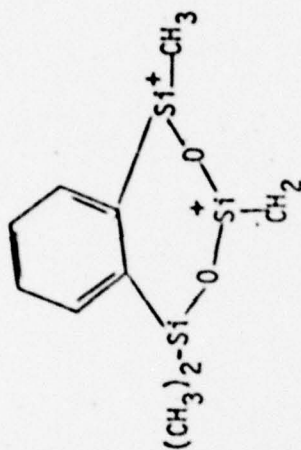
*metastable observed

SCHEME VII

TABLE I

MASS SPECTRA OF ARYLPENTAMETHYLDISILOXANES

m/e	Ph[a]	Ph-d$_5$[b]	p-tolyl[c]		m/e	Ph[a]	Ph-d$_5$[b]	p-tolyl[c]
59	4.0	4.4	3.9		183		1.9	
73	9.5	12.8	9.6		184		3.8	
89	5.0				193	11.7		3.8
89.5	1.0				194	2.3		
90	0.7				195	2.0		
91		6.3	3.6		197		9.7	
91.5		2.1			198		6.2	
92		0.8			199		1.8	
96			1.6		207			8.8
96.5			0.3		208			2.0
97	14.5		0.5		209	100.0		1.4
97.5	2.5				210	22.5		
98	1.0				211	10.0		
99.5		32.3			213		9.5	
100		6.7			214		100.0	
100.5		1.0			215		46.2	
104			5.2		216		17.9	
104.5	1.0		0.9		223			100.0
105	3.3		3.2		224	0.33		22.0
105.5	0.1				225	0.08		8.8
107		4.5			226	0.03		
107.5		0.8			229		0.7	
108		0.7			230		0.2	
110		3.6			231		0.1	
111.5			1.9		238			3.2
112		3.5	0.4		239			0.5
112.5			0.1		240			0.2
135	13.3							
136	1.8							
137	1.0							
140		22.6						
141		3.1						
142		1.5						
147	2.0							
149			11.2					
150			1.6					
151			0.5					
179	3.3							

[a]Metastables: 25-26 (73)^2/209 = 25.7; 81.5-82.5 (89)^2/97 = 81.7; 86.5-88 (135)^2/209 = 87.2; 152.5-154.5 (179)^2/209 = 153.3; 177-179 (193)^2/209 = 178.2.

[b]Metastables: 24.7-25.2 (72)^2/214 = 24.9; 82.5-84 (91)^2/99.5 = 83.2; 90.5-92.5 (140)^2/214 = 91.6; 157-159 (184)^2/214 = 158.2; 180-183 (197)^2/214 = 181.4.

[c]Metastables: 23.5-24.5 (73)^2/223 = 23.9; 88.5-88.9 (96)^2/104 = 88.6; 99-100 (149)^2/223 = 99.6; 166-168 (193)^2/223 = 167.0; 192-194 (207)^2/223 = 192.2; high resolution mass spectra calc. for $C_{10}H_{15}OSi_2$ = 207.066; found 207.067.

TABLE II

MASS SPECTRA OF IV, V, VI, VII, VIII, AND IX

m/e	IV	V	VI	VII	VIII	IX
73	4.9	3.8	11.6	6.8	11.8	
77	11.9				6.8	4.5
78	13.8				7.3	
79	3.4				5.5	
81	4.3		3.6			
82			15.1			
83		1.1	7.1			
83.5		0.9				
84		0.9	8.1			
84.5			0.9			
85			2.5			
87			5.6			
89	25.4				15.5	
89.5	4.9				2.7	
90	2.0	19.0			1.6	3.6
90.5		11.1				
91	9.8	3.5	5.2	3.0	10.5	
91.5			1.7			
92	3.2		1.7			
93	3.8				5.5	
94	6.2					
95	3.0		16.2			
96			27.9	3.6		
96.5				0.6		
97	3.0		7.0	1.0		
105	9.8			13.9	21.8	12.6
107	6.0				6.4	3.1
108		4.3	3.1			
109			9.3			
110			34.8			
111			8.3			
112			12.2			
113			3.0			
115	3.0					
117			3.6		4.2	
118				5.0		4.8
119	5.5			4.7	9.1	7.1
120	3.2				7.3	3.5
120.5					0.6	1.2
121	4.3				6.4	3.7
122		2.5	3.3			
123		2.0	12.2			
124			11.6			
125			6.2			
126			11.6			
127			6.2			
128	13.4				7.7	
128.5	3.4				1.7	
129	2.9				2.8	
131	7.4	11.7				
131.5		5.7				
132		2.8				
133			3.7	3.3		
133.5			0.5			
134			3.0	1.5		
134.5				0.5		

Table II con't.

m/e	IV	V	VI	VII	VIII	IX
135	34.0			13.7	21.8	11.6
135.5	2.0				1.9	
136	6.2		3.0		3.2	1.4
137	4.7	3.5	4.7			1.3
138		11.3	4.1			
138.5		4.6				
139		3.8	5.6			
139.5		2.6				
140			68.6			
141			4.7			
142			5.2	4.7		
142.5				1.4		
143	1.3			1.3		
143.5	0.6					
146		1.1				
146.5		0.5				
147		0.7		5.0		
149				55.3		
149.5				1.6		
150				8.9		
151				4.2		1.4
151.5						0.3
152						3.9
154						3.5
155						3.5
159						1.5
159.5						0.4
160			5.2			0.7
162			3.5			
163			6.6			4.8
164					3.6	
165						6.8
166					4.8	1.5
166.5						0.5
167			23.4			
168			8.1			
169			7.0			
172			4.3			
173			8.1			
174			7.0			
179	3.8		4.3	4.7		24.1
180					6.4	9.0
181	3.6		1.5			15.8
182			4.7		5.5	3.9
183			8.1			3.9
184			11.0			
185	13.8		3.3			
190			7.0			
193	48.9		3.0	6.1	59.1	46.2
194	11.1	4.8		1.3	12.3	19.3
195	9.1	22.2		2.8	12.7	30.6
196		19.0	3.6		3.0	5.1
197	8.5	4.8	87.2	31.6	39.1	15.8
198			22.1		9.1	3.5
199			9.3		2.4	2.5
200			5.2			
202		2.7				
203		2.9	16.2			
204			4.7			

Table II con't.

m/e	IV	V	VI	VII	VIII	IX
206			4.3			
207		5.4	12.8	73.7		
208			2.7	14.7		
209				9.2	9.1	
210					1.9	
211					1.5	
212		3.5			3.1	
214			12.8			
223				3.7		
224						3.9
225				11.1		
226				6.5		
227				1.7		
234	4.3					
240						7.1
249	5.5					
251	9.8		4.0			
255	6.2				4.9	69.4
256					1.9	17.4
257					1.0	10.0
259						13.9
260		2.5				3.5
261	4.7	3.0				
262		2.1				
263		1.0				
264			7.0			
265			4.1			
266			1.4			
271	100.0				100.0	38.1
272	26.6				26.8	10.0
273	11.7				11.8	3.9
275		12.7				
276		54.0				
277		100.0				
278		26.6				
279		11.7				
280			11.6			
281			100.0	4.2		
282			36.0			
283			14.0	7.9		
284			2.4	2.0		
285				1.5		
286	3.2				1.4	
287	1.1				0.6	
288	0.4				0.3	
290		1.8				
291		4.3				
292		6.5				
293		1.6				
294		1.3				
296			18.6			
297			5.6			
298			1.9			
299				100.0		
300				30.5		
301				11.1		

Table II con't.

m/e	IV	V	VI	VII	VIII	IX
314				8.1		
315				3.5		
316				1.2		
317						3.5
318						1.0
319						0.5
333						100.0
334						33.9
335						11.1
348						9.4
349						3.1
350						1.3

Metastables IV: 61.5-$62.2 \ (89)^2/218 = 61.9$; 111.8-$112.2 \ (179)^2/286 = 112.0$; 112.3-$112.7 \ (120)^2/218 = 112.5$; 120.8-$121.1 \ (128)^2/135.5 = 120.9$; 136-$139 \ (193)^2/271 = 137.5$; 143.2-$143.4 \ (197)^2/271 = 143.2$; 239-$242 \ (255)^2/271 = 239.9$.

Metastables V: 61.5-$63.0 \ (90)^2/131 = 61.8$; 68.5-$69.0 \ (138)^2/277 = 68.8$; 114-$115 \ (122.5)^2/131 = 114.6$; 136-$319 \ (195)^2/277 = 137.3$; 148.5-$149 \ (203)^2/277 = 148.8$; 164-$165 \ (179)^2/195 = 164.3$; 242-$247 \ (260)^2/277 = 244.0$ and $(261)^2/277 = 245.9$.

Metastables VI: 62-$63 \ (91)^2/133 = 62.2$; 77.2-$77.9 \ (84)^2/91 = 77.5$; 137-$139 \ (197)^2/281 = 138.1$; 152.5-$153.5 \ (207)^2/281 = 152.5$; 245-$252 \ (264)^2/281 = 248.0$.

Metastables VII: 61.5-$61.8 \ (96)^2/149.5 = 61.7$; 82-$83 \ (89)^2/96 = 82.5$; 126-$127 \ (134)^2/142 = 126.5$; 142-$146 \ (207)^2/299 = 143.3$; 168-$170 \ (225)^2/299 = 169.3$; 176-$181 \ (191)^2/207 = 176.2$ and $(193)^2/207 = 180.0$; 265-$270 \ (283)^2/299 = 267.9$.

Metstables VIII and Peak Matching: 61.5-$62.0 \ (89)^2/128 = 61.9$; 112-$114 \ (120)^2/128 = 112.5$; 119-$121 \ (128)^2/135.5 = 120.9$; 127.5-$129 \ (135.5)^2/143 = 128.4$; 136-$138.5 \ (193)^2/271 = 137.5$; 236-$242 \ (255)^2/271 = 239.9$; high resolution mass spectra calc. for $C_9H_{13}OSi_2$ 193.050; found 193.052.

Metastables IX and Peak Matching: 54.5-$54.8 \ (135)^2/333 = 54.7$; 90-$91 \ (120)^2/159 = 90.6$; 137-$138 \ (193)^2/271 = 137.5$; 150-$153 \ (159)^2/166.5 = 151.8$; 195-$197 \ (255)^2/233 = 195.3$; 300-$302 \ (317)^2/333 = 301.8$; high resolution mass spectra calc. for $C_{14}H_{15}OSi_2$ 255.066; found 255.068.

TABLE III

MASS SPECTRA OF 1,1,3,3,5,5-HEXAMETHYL-1,5-DIARYLTRISILOXANES

m/e	Ph[a]	Ph-d3[b]	Ph-d5[c]	p-tolyl[d]	m/e	Ph[a]	Ph-d3[b]	Ph-d5[c]	p-tolyl
73	9.6	9.1	14.6	12.1	149				54.2
					150				9.2
75				3.0	151				10.8
77				4.0					
78				4.1	157	3.0			
91	3.1		5.6	14.2	159		0.6		
92				4.0	159.5		1.6		
					160		1.4		
96			3.4	4.0	161.5		0.4	2.4	
					162			2.4	
103				4.3					
					165	17.9			
105	3.0			14.2	165.5	5.1			
					166.0	3.1			
107	3.0								
108		1.9			167		2.2		
					167.5		8.2		
110			3.9		168		18.6		
					168.5		6.8		
112			3.4		169		2.7		
					169.5			4.1	
118				5.4	170			46.3	
119	3.1			7.5	170.5			13.4	
					171			6.8	2.1
121	3.0			6.7	171.5				0.7
					172				0.5
126	7.2	0.8	3.5						
126.5	2.1	1.1			179				17.1
127	1.1	5.0			179.5				6.7
127.5		5.0			180				3.5
128		1.8	12.2						
128.5			4.1		193	8.5			3.8
129.0			2.1						
					195	8.9	3.2		
131	3.8			3.0	196	5.1	3.1		7.3
					197	16.2	1.8	13.4	
133	3.5	0.7	3.9	16.7	198	3.4	1.9	3.7	
133.5				3.8	199	1.3		1.7	
134				2.4					
135	34.0			8.3	202		9.5		
136	4.3				203		13.9		
137	3.4	9.1			204		3.2		
138		36.4							
139		5.5	4.3		206			4.1	
140	4.3	3.4	80.5		207			43.9	20.8
141			10.0		208			8.0	5.8
142			3.9		209			2.0	6.3
145				5.4	223				7.7
147				4.6					

m/e	Ph[a]	Ph-d$_3$[b]	Ph-d$_5$[c]	p-tolyl[d]	m/e	Ph[a]	Ph-d$_3$[b]	Ph-d$_5$[c]	p-tolyl[d]
225				43.8	345	100.0			
226				11.3	346	33.2			
227				1.7	347	13.6			
					348	4.7			
251	3.4				349		11.4		
253		2.4			350		47.4		
254		2.5			351		100.0		
255			7.1		352		36.4		
256			2.7		353		14.5		
257			1.2		354		3.2	19.5	
					355			100.0	
265				5.4	356			75.6	
266				1.5	357			35.4	5.0
267	20.0			1.8	358			7.3	1.8
268	6.8				359				1.0
269	1.7	5.9			360	5.1			
270		5.5			361	1.3			
271		2.1	13.2		362	0.9			
272			4.6						
273			2.0		365		0.2		
					366		0.2		
281				29.2	367		0.1		
282				10.0	368		0.1		
283				6.3	369			0.1	
					370			2.0	
297				6.7	371			0.8	
					372			0.7	
					373				100.0
					374				37.5
					375				17.5
					376				4.6
					388				3.8
					389				1.3
					390				0.9

[a] Metastables: 52.5-53.0 $(135)^2/345 = 52.8$; 96-97 $(126)^2/165 = 96.2$; 112-113 $(197)^2/345 = 112.5$; 134-136 $(193)^2/267 = 135.2$; 149-150 $(157)^2/165 = 149.4$; 205-208 $(267)^2/345 = 206.6$, 310-315 $(329)^2/345 = 313.7$.

[b] Metastables: 54-55 $(138)^2/351 = 54.2$; 96-98 $(127)^2/168 = 96.0$; 116-118.5 $(203)^2/351 = 117.4$, 150-153 $(159.5)^2/168 = 151.4$; 205-207 $(269)^2/351 = 206.2$; 236-239 $(253)^2/269 = 237.9$.

[c] Metastables: 54.5-56 $(140)^2/355 = 55.2$; 96-98 $(128)^2/170 = 96.4$; 120-122 $(207)^2/355 = 120.7$; 205-208 $(271)^2/355 = 206.9$; 238-242 $(255)^2/271 = 239.9$; 319-324 $(338)^2/353 = 321.8$.

[d] Metastables: 98-100 $(133)^2/179 = 98.8$; 134-137 $(255)^2/373 = 135.7$; 162-165 $(171)^2/179 = 163.4$; 211-213 $(281)^2/373 = 211.7$; 340-342 $(357)^2/373 = 341.7$.